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Montmorillonite: An Introduction to Properties and Utilization

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Abstract

Clay mineral is an important material available in nature. With an increasing understanding of clay structure, montmorillonite is realized viable for an enhanced performance in a variety of materials and products in the areas of catalysis, food additive, antibacterial function, polymer, sorbent, etc. Significant development in the use and application of montmorillonite is seen in recent time. This chapter provides an overview of montmorillonite, structure, and properties and particularly discusses its recent utilization in important materials. Montmorillonite is introduced in terms of its natural sources, chemical structure, physical and chemical properties, and functional utilization. The important physical and chemical properties are summarized as particle and layered structure, molecular structure and cation exchange effect, barrier property, and water sorption. This is followed by the important functional utilizations of montmorillonite based on the effects of its chemical structure. The important functional utilization of montmorillonite includes food additive for health and stamina, for antibacterial activity against tooth and gum decay, as sorbent for nonionic, anionic, and cationic dyes, and the use as catalyst in organic synthesis. The environment concerns, to date, do not indicate the adversity for particles used as additive. Studies will be useful which are clearly based on any montmorillonite structure to describe environmental effects.

Keywords: clay, montmorillonite, bentonite, water, cationic exchange

1. Introduction

Historically, clay mineral has long benefitted human life and civilization. Being an integral part of earth, its history is older than the creation of man. The divine script of Holy Quran confirmed that man was created using clay. This indicates that clay mineral was present before

the human life began on earth. The ancient Greek philosophy and culture consider clay an important component of life. Currently, the twenty-first century is in the process of appreciating the even growing number of clay applications in material science.

In times when technology was not at the core of human civilization, clay mineral was used as an important form of material to form a variety of products. Its softness, plasticity, porosity, tangibility, pliability, and climatic adaptability, all at affordable cost, were viable characteristics to recognize its usefulness, and introduced several products.

Today, when nanotechnology is the hallmark of scientific world, the contribution of clay mineral is significantly visible as highly useful fillers or additives in polymers for desired effects. Nanoclays, based on montmorillonite, are currently used to modify the polymer performance.

The science of clay was introduced since prehistoric times. Ceramists used nanoparticles since antiquity [1]; however, nanotechnology is the knowingly scientific utilization of nanoparticles. The use of kaoline may be traced back to the third century BC in China. China clay, a traditional name of kaoline, is a mixture of minerals generally containing kaolinite, quartz, mica, feldspar, illite, and montmorillonite [2].

Historically, the use of clay is known in architecture, industry, and agriculture. The production of sun-dried and fired bricks for building construction still follows century-old procedures. Floor tiles, ceramics, earthenware, and pipes for drainage are examples of clay-based products used since ages. An interesting behavior of clay, in producing products, is its ability to swell and to mold in water, and retain the shape of a container when dry.

A common characteristic of clay mineral is a fine-grained natural structure in a sheet-like geometry. The sheet-structured hydrous silicates are generally called phyllosilicates [3]. The natural clay particle is smaller than 0.004 mm in diameter that may range from 0.002 to 0.001 mm for quartz, mica, feldspar, iron, and aluminum oxides [4]. Colloidal clay particles are finer and found in layered silicates (<0.001 mm in diameter).

Clay minerals may be grouped in four types, shown in **Table 1**. The group members vary mainly in the layered structure. These include the kaolinite group, the smectite group (montmorillonite group), the illite group, and the chlorite group [5].

The kaolinite group has three members including kaolinite, dickite, and nacrite; the formula for kaolinite group is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.

The illite group is represented by mineral illite, the only common clay type. The general formula for illite is $(\text{K}, \text{H})\text{Al}_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot \text{XH}_2\text{O}$. It is an important rock-forming mineral and main component of shales. The structure of this group is similar to the montmorillonite group with silicate layers sandwiching an aluminum oxide/hydroxide layer in the same stacking sequence.

The chlorite group is relatively large. This group is not necessarily considered as part of clays; therefore, it is placed as a separate group in phyllosilicate. The members in chlorite group are mesite, chamosite, cookeite, and daphnite with varying formulas and structures. There is no general formula.

The variety of clay minerals is based on the arrangement of tetrahedral and octahedral sheets. For example, 1:1 clay mineral would have one tetrahedral and one octahedral sheet per clay

S. no	Group name	Member minerals	General formula	Remarks
1.	Kaolinite	Kaolinite, dickite, nacrite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Members are polymorphs (composing of the same formula and different structure.
2.	Smectite	Montmorillonite, pyrophyllite, talc, vermiculite, sauconite, saponite, nontronite	$(\text{Ca, Na, H}) (\text{Al, Mg, Fe, Zn})_2 (\text{Si, Al})_4 \text{O}_{10}(\text{OH})_2 \cdot \text{XH}_2\text{O}$	"X" indicates varying level of water in mineral type.
3.	Illite	Illite	$(\text{K, H})\text{Al}_2 (\text{Si, Al})_4 \text{O}_{10}(\text{OH})_2 \cdot \text{XH}_2\text{O}$	"X" indicates varying level of water in mineral type.
4.	Chlorite	i. Amesite, ii. Chamosite, iii. Cookeite, iv. Nimite, and so on	i. $(\text{Mg, Fe})_4 \text{Al}_4 \text{Si}_2 \text{O}_{10}(\text{OH})_8$ ii. $(\text{Fe, Mg})_3 \text{Fe}_3 \text{AlSi}_3 \text{O}_{10}(\text{OH})_8$ iii. $\text{LiAl}_5 \text{Si}_3 \text{O}_{10} (\text{OH})_8$ iv. $(\text{Ni, Mg, Fe, Al})_6 \text{AlSi}_3 \text{O}_{10}(\text{OH})_8$	Each member mineral has a separate formula. This group has relatively larger member minerals and sometimes considered as separate group not as part of clays.

Table 1. Major groups of clay minerals [5].

S. no	Clay mineral group	Layer type	Layer charge
1.	Kaolinite	1:1	<0.01
2.	Montmorillonite or smectite	2:1	0.5–1.2
3.	Illite	2:1	1.4–2.0
4.	Vermiculite	2:1	1.2–1.8
5.	Chlorite	2:1:1	Variable

Table 2. Sheet structure for the layers of clay minerals [7].

layer; 2:1 clay mineral would contain two tetrahedral sheets and one octahedral sheet sandwiched between the two tetrahedral sheets (montmorillonite is an example of clay mineral having 2:1 sheet structure); and 2:1:1 clay minerals are composed of an octahedral sheet adjacent to a 2:1 layer [6]. The sheet structure for the layers of various clay minerals with the possible charge is shown in **Table 2** [7].

Natural reserves of montmorillonite are present in various parts of the world. An earliest discovery of montmorillonite was indicated in 1847 in Montmorillon in the Vienne prefecture of France. However, the use of montmorillonite for medicinal purposes may be in over 200 cultures including the ancient Egyptians, pre-Aztec Amargosians, natives of Mexico, South Americans, and North Americans [8].

The names used for montmorillonite are known in different languages, including montmorillonita (Portuguese, Catalan, and Spanish), montmorilloniet (Dutch), and montmorillonit (German, Hungarian, Slovak) [9].

The major montmorillonite deposits found at five places include Himalayas (China), Urals (Pakistan), Caucasians (Georgia, Russia), Andes (Peru, Ecuador), and Wasatch (UT, USA) [10].

2. Bentonite

Bentonite is an important rock of clay found in nature. It is an important source of montmorillonite in nature. It is a rock formed of highly colloidal and plastic clays mainly composed of montmorillonite [2]. In addition to montmorillonite, bentonite may contain some amount of crystalline quartz, cristobalite, and feldspar.

The variety of bentonite applications are the result of its useful and interesting chemical and physical properties. This range of properties include rheology, sorbent effects, plasticity and lubricity, high dry bonding strength, high shear and compressive strength, impermeability, and low compressibility [11].

Natural bentonite particles are indistinguishable from kaolin clay minerals viewed under scanning electron microscope; however, the main difference indicated was thickness. Sodium or potassium salts of bentonite exfoliate into thin plates that could be of 1 nm in thickness theoretically [12].

In general, the clay minerals based on bentonite may exhibit the properties of thixotropic gel formation with water, high water absorption, and high cation exchange capacity (CEC). These properties could be varied in clay minerals depending upon the nature of interstitial water and exchangeable cations in the interlayer space.

Bentonite, which mainly contained montmorillonite, was discovered in about 1890 in USA, and the name “bentonite” is associated with the name of an American geologist for the one time Fort Benton in the eastern Wyoming Rock Creek area, USA [2].

Montmorillonite derived from bentonite may contain sodium or calcium. Sodium montmorillonite is the main fraction in bentonite found in combination with 10–20% of various minerals including feldspar, calcite, silica, and gypsum [10].

3. Montmorillonite structure

The physical structure of montmorillonite particle is generally perceivable in sheets and layers. Each layer is composed of two types of structural sheets: octahedral and tetrahedral. The tetrahedral sheet is composed of silicon-oxygen tetrahedra linked to neighboring tetrahedra by sharing three corners resulting in a hexagonal network. The remaining fourth corner of each tetrahedron forms a part to adjacent octahedral sheet. The octahedral sheet is usually composed of aluminum or magnesium in sixfold coordination with oxygen from the tetrahedral sheet and with hydroxyl. The two sheets together form a layer. Several layers may be joined in a clay crystallite by interlayer cations, by Van der Waals force, by electrostatic force, or by hydrogen bonding.

Theoretical formula and structure is indicated in **Figure 1** [13]. The important natural physical properties of montmorillonite are given in **Table 3**. The best field indicators are softness, color, water, soapy feel, and expansion with water absorption.

The variation in the chemical formula of montmorillonite is possible resulting from the modifiable structure. The cation substitution introduces charge imbalance. Therefore, the chemical composition can vary. The exact theoretical formula is never seen in nature [13]. However, the structure in nature in any form consists of water molecules.

The chemical formula for montmorillonite discovered at Montmorillon, France, is $(\text{Ca}_{0.14}\text{Na}_{0.02})_{\Sigma=0.16}(\text{Al}_{1.66}\text{Mg}_{0.36}\text{Fe}_{0.04})_{\Sigma=2.08}(\text{Si}_{3.90}\text{Al}_{0.10})_{\Sigma=4.00}\text{O}_{10}(\text{OH})_2 \cdot 1.02\text{H}_2\text{O}$.

The oxide composition comprises silicon and aluminum oxides; however, it was predominantly calcium montmorillonite discovered at Montmorillon. The dominant fractions were SiO_2 and Al_2O_3 , where SiO_2 was slightly more than the 50% of total oxides.

The elementary molecular structure is based on units comprising silica tetrahedron and aluminum octahedral. The cation Si^{+4} is fourfold and possesses tetrahedral coordination with oxygen, while the cation Al^{+3} occurs in sixfold or octahedral coordination.

A layered structure is influenced by the presence of charge in tetrahedral and octahedral sheets. Isomorphous substitution in clay mineral mainly produces charge. Isomorphous

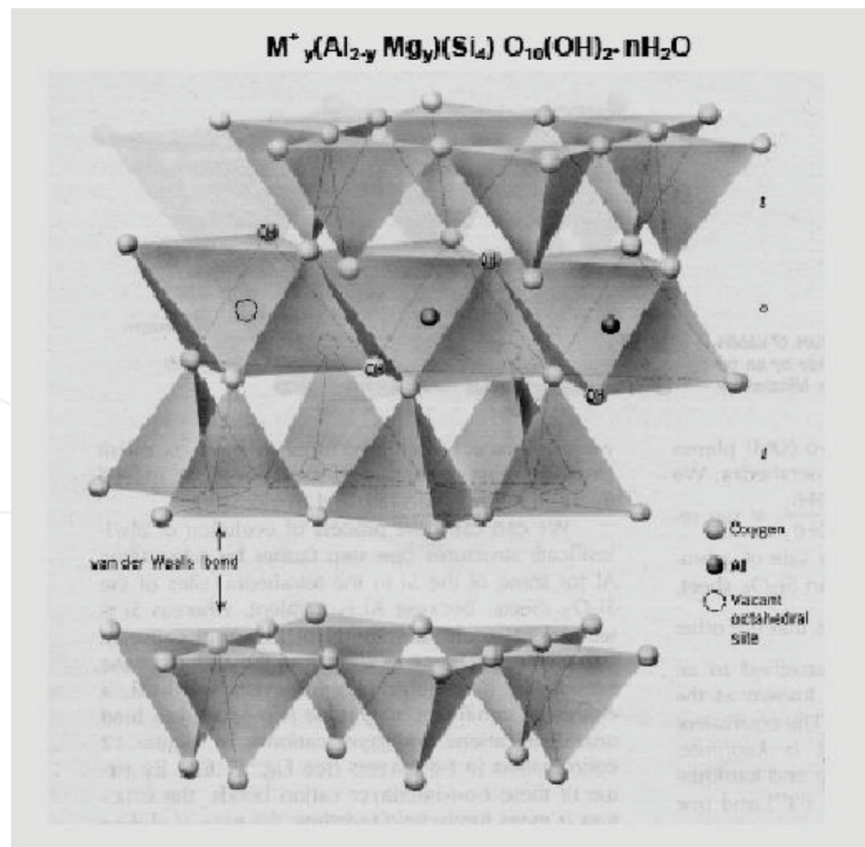


Figure 1. Theoretical formula and structure of montmorillonite (source: Nanocor Inc., IL (USA) [13]).

S. no	Property name	Description
1.	Density	2–3 g/cm ³ (measured)
2.	Crystal system	Monoclinic
3.	Hardness	1–2 on Mohs scale, soft, possess fine-grained occurrence
4.	Fracture	Irregular, uneven
5.	Cleavage	Perfect
6.	Luster	Earthy, dull
7.	Transparency	Translucent
8.	Color	White, buff, yellow, green, rarely pale pink to red (presence of high valance Mn produces pink to red coloration)

Table 3. Important natural physical properties of montmorillonite [9].

substitution is the replacement of an element with another element in mineral crystal without modifying its chemical structure. For example, Al^{3+} can replace Si^{+4} in tetrahedral coordination and replacement of Al^{3+} is possible by Mg^{2+} , Fe^{2+} , Fe^{3+} in octahedral coordination.

The sheets present in montmorillonite are composed of 2:1 structure. The sheets in the crystal plane have a negative charge and hydroxyl groups linked to aluminum or magnesium. The electrostatic force is primarily the force of attraction between the sheets; however, it is fragile.

Chemical composition, ionic substitution, layer structure, and particle size of natural clay minerals have important role in creating a variety of minerals with specific characteristics. However, sheet structure was used to classify the clay minerals, and chemical composition was used for nomenclature.

4. Montmorillonite in nanoclay

Montmorillonite is the basic raw material used in producing nanoclay. Chemically, it can be described as hydrated sodium calcium aluminum magnesium silicate hydroxide, $(\text{Na}, \text{Ca})_{0.33}(\text{Al} \text{ Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \text{ nH}_2\text{O}$ [8]. The interaction between nanoclay particles and polymer matrix significantly depends upon the hydroxyl groups and charges present in the nanoclays particle.

In clay-polymer system, the clay nanoparticle can be intercalated or exfoliated. Where clay crystal is used as nanoparticle, it can be referred as intercalated clay (in this case, the polymer chains are between the clay platelets), and when the single particle of clay is the constituent unit, it is referred as exfoliated (i.e., clay platelets are isotropically dispersed in polymer). The important required characteristics include are particle size, surface area, and aspect ratio.

The length and breadth of the particles can range from 1.5 μm down to few tenths of a micron [14]. The third dimension of particle, in the study, is described as thickness, width, or diameter; however, diameter may be used. The diameter of the particle is exceptionally smaller relative

to its length, measuring to only one-billionth part of a meter ($=1$ nm). Therefore, an extremely high average length-to-diameter ratio (called aspect ratio) of 200–500 is achievable.

An increased aspect ratio produces a higher surface area. A smaller mass of nanoclay shows a high surface area, for example, typically 1 g of a nanoclay product is known to have a surface area in excess of 750 m^2 [15]; that is an equivalent area to nine soccer fields [16].

Nanoclays are available containing over 98% montmorillonite. The variable colors are the result of substitution of interlayer-cations by iron, titanium, and manganese within the lattice structure and depend upon the level of substitution and valence state of cations [13].

Montmorillonite is required to be surface modified to become organophilic and easy to disperse in polymers. Organophilic montmorillonite is produced using organic cation substitution.

The progress in the study to modify the structural composition of montmorillonite, its processing, and surface treatment may be indicated by the achievement of 40 patents issued to one commercial organization [17]. Montmorillonite nanoclay has experienced a variety of utilizations.

Montmorillonite nanoclay is indicated as a drug carrier system and as an additive. Montmorillonite composite for application in drug system can be produced through the utilization of anionic, cationic, and nonionic surfactants to enhance basal spacing resulting in organoclay to be used in drug loading and drug release. Important aspects in a drug carrier system including drug entrapment, molecular level interactions, analysis for a sustained drug release, and targeted drug release are reviewed [18].

This review discussed various aspects of montmorillonite nanoclay such as structure, properties, multifarious applications, and the results of biocompatibility studies.

Significantly rich intercalation chemistry at a reduced cost is an important reason in producing montmorillonite-polymer nanocomposites. Such hybrid materials, also termed as polymeric nanocomposites (PNC), received extensive interest in research and industry. PNC materials on the nanoscale level exhibit advantageous effects in mechanical properties, heat distortion temperatures, thermal stability, flame retardancy, and enhanced barrier properties.

Commercially, several desired effects obtained in PNC are resulting in an increasing consumption of montmorillonite. The combination of improved properties, including the weight reduction and low cost in the final product, resulted in important commercial applications in automotive and packaging, and so on. The significant findings in the montmorillonite-polymer nanocomposites are reviewed for material types: elastomers, thermosets, and polymers from natural resources or biopolymers [19].

The volume of recent research literature clearly indicates the interest and growing consumption of clay minerals particularly montmorillonite. In addition to natural montmorillonite applications, the studies are concentrating in the development of montmorillonite as nanoclay/organophilic clay through modifications in its physical and chemical structures. The utilization of nanoclay is discussed in the following sections where performance effects of montmorillonite are described.

5. Functional properties

5.1. Cation exchange property

Cation exchange capacity is a property of soil introduced by clay and organic matters. It is the capacity of soil to hold cations (generally Al^{3+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} , Na^+ , K^+ , H^+) [20] and described as the quantity of positively charged ions held by the negatively charged surface of clay minerals. It may also be termed as cation exchange capacity (CEC) that may be measured as a centimol positive charge per kg of soil or milli-equivalent (meq) of positive charge per 100 g of soil.

Fine-grained particles of clay result in an increased surface area per unit mass. Smaller particle size (0.002–0.001 mm in diameter) results in a significantly higher surface area, where a large number of cations can be adsorbed. These adsorbed cations impart significant level of electrical conductivity in clay [21].

Ionic substitution in the sheet structure produces useful modifications. Ions like Fe^{3+} and Al^{3+} are small enough to enter the tetrahedral coordination with oxygen and substitute Si^{4+} . Similarly, cations like Mg^{2+} , Fe^{2+} , Fe^{3+} , Li^+ , Ni^{2+} , and Cu^{2+} can substitute Al^{3+} in the octahedral sheet [22]. Large-sized cations such as K^+ , Na^+ , and Cs^+ are located between the layers and referred as interlayer cations.

5.2. Electrical conductivity

Clay particles are the porous materials. The pore fluid influences the electrical conductivity. The electrical conductivity (mS/m) of a porous material is the combination of electrical conductivities of the matrix material and the pore fluid [23].

Air, water, or saline water may be present in the pore. When the pore fluid is of low conductivity, for example, air or water, the bulk conductivity of clay mineral is contributed by the matrix material. Pore fluid having a higher electrical conductivity significantly enhances the total electrical conductivity of clay, for example, clay particles with a significant porosity level (40–50%), and saline water present in the pore; then the bulk conductivity is mainly the contribution of pore fluid. In this case, there would be negligible difference in the conductivities of sand and clay.

A higher content of clay particles with 2:1 structure present in montmorillonite sample produces an increased bulk electrical conductivity for non-saline soils [24]. This effect was attributed to the exchangeable cations or to proton transfer from the dissociation of interlayer water content. A reduced level of interlayer water contents in K-saturated clays resulted in the lowest electrical conductivity.

Since the clay content, pore fluid, clay type, saline water, and water saturation influence the soil conductivity, the assessment of electrical conductivity of reservoir rock may be used to estimate these factors [25]. However, the variation in the distribution of liquid and solid phases introduces the variation and complication in the electrical conductivity of heterogeneous porous medium.

The distribution of electrical ions around clay pores is called membrane polarization. In membrane polarization, the negative ions are oriented to one end of the pore under the influence of DC potential across the clay pore, and this polarization resists the current flow.

In the study of soil, the clay content in soil can be determined using electrical conductivity and membrane polarization as the function of clay content.

5.3. Heat resistance

Montmorillonite is a good heat insulator, and heat-resistant effects are obtainable using it as an additive in any substance. This is an area of significant research to produce thermal barrier effects in composite material structure.

Thermal barrier properties of clay minerals had been used in heat-resistant and flame-retardant applications. Nanoclay is currently used extensively and investigated in polymer composite to obtain an increased thermal stability and flame retardancy.

The variation in the expansion, under heat effects, for metals, polymers, and ceramics had been noted. Generally, the order of thermal expansion magnitude in polymer, metal, and ceramic may be indicated as follows:

$$\text{Polymer} > \text{metal} > \text{ceramic}.$$

This relative order is based on the values of linear thermal expansion coefficient which are in the range of 20–100, 3–20, and 3–5 ppm/°C for polymers, metals, and ceramics, respectively [26].

Therefore, an increased thermal stability of montmorillonite introduces its use as a filler in producing polymers to impart a low thermal expansion. However, enhancement in polymer thermal stability requires an increasing aspect ratio, and an aspect ratio of greater than 100 is useful.

5.4. Water sorption

Water sorption is an important characteristic of natural clay particles. Clay particles can absorb or lose water in response to changes in humidity content in the ambient environment; when water is absorbed, it fills the spaces between the stacked silicate layers [27].

Montmorillonite typically exhibits a gradual dehydration and phase change to a stronger nonexpendable clay. The specific gravity of any type of clay is variable resulting from loss or gain of water. Most of the known clay types are available in nature as a mixture containing several varieties including carbonates, feldspars, micas, and quartz.

Several studies addressed the swelling behavior of montmorillonite. The interaction of montmorillonite with water introduces useful effects. Water molecules cause swelling in montmorillonite. This swelling is a result of complex montmorillonite-water interactions between particles and within the particle itself.

Water molecule adsorption and swelling of montmorillonite introduce hydrated states and hysteresis. The migration of counter-ion, initially bound to montmorillonite surface to the central interlayer plane, leads to swelling in montmorillonite. Therefore, charge locus in montmorillonite has a strong influence on swelling dynamics [28].

An important concern in clay mineral study is how the monovalent and divalent cations affect the swelling pattern of K^+ , Na^+ , and Ca^{2+} -montmorillonites.

Montmorillonite is a 2:1 clay mineral; that is, two tetrahedral sheets separated by one octahedral sheet. The montmorillonite platelets can be negatively charged when

- i. tetrahedral substitution of Si by Al in two tetrahedral sheets, or
- ii. octahedral substitution of Al by Mg in central octahedral sheet.

In any of the above two (i and ii) cases, negative charge produced is compensated by interlayer ions. The hydration of interlayer cations produces swelling [29].

The small platelet size and stacking structure are indicated as complicated to accurately characterize through experiment. Therefore, molecular dynamic simulation (MDS) is a useful way of understanding the atomic level structure. MDS is useful to study montmorillonite structure including swelling and hydration of interlayer cations. MDS was performed for K^+ , Na^+ , and Ca^{2+} -montmorillonites with varying level of water content.

The valence of the cations showed a significant influence on montmorillonite-water system. Simulations indicate that the cation K^+ shows a strong interaction with dehydrated montmorillonite sheets; however, in case of hydrated montmorillonite sheets, cation Ca^{2+} interacts strongly. Therefore, the layer spacing of simulated K^+ , Na^+ , and Ca^{2+} -montmorillonites was obvious.

The simultaneous measurement of swelling and swelling pressure was done using a researcher-developed cell [30]. Undisturbed clay samples at a defined swelling (0–75%) were removed from the cell and analyzed using SEM, FTIR, and ATR (micro-attenuated total reflectance) spectroscopy. Silicate (Si-O)-stretching region ($1150\text{--}950\text{ cm}^{-1}$) showed significant changes with variation in swelling and orientation. It was found that the reduced particle size with increased swelling was related to increased misorientation of the clay platelets. The rearrangement of clay platelets was observed as a direct result of the breakdown of the clay particles with increased hydration.

6. Functional utilization

The addition of montmorillonite in material, polymer, and products may result in significant enhancement in the required performance. Interestingly, there is a great variety of montmorillonite utilization as an additive in composite or as a functional filler in polymers. The results obtained indicated useful effects. Examples included the applications as food additive for health and stamina, for antibacterial activity, as sorbent for nonionic, anionic, and cationic dyes, and as catalyst in organic synthesis, and so on.

The variety of montmorillonite utilization in material and product performance is significant in recent literature. The following sections describe the important useful effects that are obtainable using the selected type of montmorillonite.

6.1. Resistant to nausea and diarrhea

Dietary toxins, bacterial toxins, and metabolic toxins can be absorbed by clay to resist nausea, vomiting, and diarrhea. Montmorillonite-based product is indicated to work immediately on the digestive channel and bind the toxic substances resulting in their removal from the body through the stool [31].

The effects of montmorillonite-zinc oxide hybrid on diarrhea, intestinal permeability, and morphology were investigated on a total of 180 piglets. Piglets were divided in five groups and studied for 2 weeks using dietary treatment with montmorillonite and montmorillonite-ZnO in diet. Importantly, results obtained indicated that the dietary addition of 500 mg/kg of Zn from MMT-ZnO was similar to 2000 mg/kg of Zn from ZnO, and more effective relative to montmorillonite alone or 500 mg/kg of Zn, from ZnO, for the growth enhancement of piglets, alleviating diarrhea, improving intestinal microflora, mucosal barrier integrity, and morphology of weaned pigs [32].

6.2. Supportive to health and growth

The use of calcium montmorillonite (Nova Sil clay type) in human diet can diminish health-harming effects of aflatoxin-contaminated food. The study was based on a clinical trial of selected volunteers in the age range of 20–45 years. It included 23 males and 27 females. The volunteers received calcium montmorillonite low dose (1.5 g/day) and high dose (3 g/day) for weeks. The compliance to study trial by the volunteers was indicated as 99.1%.

Laboratory analysis of blood and urine samples was performed prior and after trial. Hematology, liver and kidney function, electrolytes, vitamins A and E, and minerals were not significantly changed in any study group. The study indicated the protection of participant from adverse effects of aflatoxins [33].

Montmorillonite can be the source of mineral for bacterial nutrition and found to maintain the pH levels required for a sustained growth [34]. Several bacterial species differing in morphology, motility, and Gram reaction were assisted in respiration by montmorillonite. The research results obtained show the relationship between clay minerals (montmorillonite and kaolinite), and population growth and ecology of microorganism in natural habitat.

6.3. Resistance to tooth decay

Another important obtainable effect is the resistance to tooth decay. Tooth decay can be resisted by filling micro-pore using a fluid resin which polymerizes *in situ* and creates a micro-mechanical interlock in the tooth structure. This bonding process is a selective substitution for tooth minerals. The use of montmorillonite as a reinforcing filler for dental adhesives (typically methacrylate monomers with solvent and a photo initiator) may be possible.

Results obtained for flexural strength, elasticity modulus, tensile strength, and thermal resistance on the applied dental adhesive, using montmorillonite as an additive, were encouraging. Adhesive produced with dimethacrylate copolymer and montmorillonite (0.2% concentration) showed significant performance as a dental adhesive. Improved performance obtained using 0.2% concentration of montmorillonite, indicated by X-ray diffraction (XRD) test results, was attributed to its exfoliated morphology. The resulting dental adhesive reduces the weakening of tooth structure. However, the highest concentration of 1.5% produced agglomerated clay and no significant performance enhancement [35].

The use of montmorillonite as a filler may be possible in any of the following morphologies:

- i. Agglomerated particle comprising the particle with a joined layer structure. The surface particle interacts with a polymer or a substrate.
- ii. Intercalated form, where a polymer or a substrate molecule can be between platelets.
- iii. Exfoliated form where platelets are isotropically dispersed in polymer or substrate molecules.

6.4. Drug delivery system

Adsorption and swelling characteristics of montmorillonite are useful in drug delivery systems. An increased adsorption capacity provides improved drug entrapment and sustained release of pharmaceutical drugs. Solubility, dissolution rate, adsorption, and bioavailability of hydrophobic drugs are enhanced by montmorillonite. The effects of montmorillonite in improving the drug delivery system were reviewed [36].

6.5. Adsorption of dyestuff

Effluent loading, from dyeing industries and textile-processing units, to natural environment is a serious concern. Technological solution is required to remove residual dye content from the used water. The application of montmorillonite as an adsorbent for cationic dye is an important effect. The removal of cationic dye, methylene blue, from water is achievable through adsorption process. Montmorillonite concentration used for the removal of cationic dye depends upon the initial dye concentration, contact time, solution pH, and temperature. Results obtained on dye adsorption demonstrated the equilibrium data follow the Langmuir isotherm equation [37].

Thermodynamic study of methylene blue adsorption on montmorillonite indicates that the process is endothermic revealed by the determination of enthalpy, entropy, and Gibb's free energy. Importantly, the results support the possibility of using montmorillonite as low-cost adsorbent for wastewater treatment containing cationic dyestuff. There is a large number of textile dyeing industries, in India, Pakistan, and China, that release used dye bath water containing cationic dyestuff. Adsorption system developed using montmorillonite can be useful for water recycling in dyeing industries.

Possibly, montmorillonite can be used to influence the optical, chemical, and spectral characteristics of cationic dyes. The layer charge of montmorillonite can affect the cationic dye molecular aggregation. The subject was reviewed through the research literature discussing dye reaction with clay minerals [38].

6.6. Adsorption of toxic heavy metals

An important application of adsorption properties of montmorillonite is seen in the removal of toxic heavy metals from aqueous solution. The adsorption studies using montmorillonite and kaolinite for the removal of toxic metals including As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Zn were reviewed [39].

Montmorillonite and its modified forms exhibited a significantly increased metal adsorption capacity relative to kaolinite and modified kaolinite. The modified clay mineral form was produced by pillaring montmorillonite or kaolinite by using polyoxy cations including Zn^{4+} , Al^{3+} , Si^{4+} , Ti^{4+} , Fe^{3+} , Cr^{3+} , or Ga^{3+} . The modified form can also be produced using quaternary ammonium cations including tetramethylammonium-, tetramethylphosphonium-, and trimethylphosphonium-, $\text{N}^{\text{-}}$ -didodecyl-N, $\text{N}^{\text{-}}$ -tetramethylethanediammonium, etc.

Montmorillonite modified using sodium dodecylsulfate (SDS) can remove Cu^{2+} and Zn^{2+} by sorption from aqueous solutions. The study was conducted as a function of solution pH, solute concentration, and temperature (25–55°C). The thermodynamic parameters (ΔH° and ΔS°) for Cu^{2+} and Zn^{2+} sorption on modified montmorillonite were evaluated. The study finds out that the kinetics for the sorption of Cu^{2+} and Zn^{2+} was assessed and the pseudo-first-order rate constant was evaluated [40].

6.7. Montmorillonite in biopolymer

Biopolymer modification using montmorillonite as nanofiller is found to improve the thermo-mechanical properties. Biopolymer produced from chitosan/montmorillonite nanocomposite through diluted acetic acid used as solvent for dissolving and dispersing chitosan and montmorillonite.

Pure chitosan was compared with chitosan-montmorillonite nanocomposite with and without acetic acid in terms of morphological structure and selected properties. Results obtained in XRD and TEM indicated an intercalated and exfoliated nanostructure at a reduced montmorillonite loading and an intercalated and flocculated nanostructure at an increased montmorillonite loading.

Thermal stability and mechanical properties were determined using TGA and nanoindentation. Thermal stability, hardness, and elastic modulus of nanocomposite matrix improve with the increasing loading of nano-dispersed montmorillonite. Crystallinity, thermal stability, and mechanical properties may be influenced by acetic acid residue in chitosan matrix [41].

The study of montmorillonite in potato starch showed the improvement in thermal and Young modulus properties. Nanocomposite films of glycerol-plasticized starch/ montmorillonite were produced. Three different loadings of montmorillonite aqueous suspension were applied to potato starch.

Dispersion of montmorillonite in starch was studied using X-ray diffraction (XRD). Results indicated that the nanomontmorillonite formed an intercalated structure and complete exfoliation was not observed under the experimental conditions used. Thermogravimetric analysis indicated the enhancement in the thermal resistance with the increased loading of montmorillonite; however, the water absorption by the starch-montmorillonite nanocomposite, at 75%

constant relative humidity, was reduced. The result of micro-tensile test of nanocomposite film showed that Young modulus improved up to 500% at 5 wt.% of montmorillonite [42].

6.8. Effects in fiber-forming polymer

Important properties of fiber-forming polymers may be improved using montmorillonite as a filler [43]. In general, clay mineral (nm) showed flame-retardant effects as assessed by a reduction in the peak heat release rate for various thermoplastic polymers including polystyrene, polyamide-6, polypropylene, polyamide-12, poly(methyl methacrylate), polyethylene, and ethylene vinyl acetate (EVA).

Montmorillonite-nylon-6 (nm) composite was produced through melt bending or compounding technique followed by injection molding using percent loading of organo-montmorillonite (nm) composites ranging 0–5 wt.% content. The desired properties of tensile and flexural properties were indicated optimum at 5 wt.% loading. Other improvement observed includes storage modulus, stiffness, and heat distortion temperature, and the reduction in water absorption relative to virgin nylon-6.

Nanometer-sized particles of montmorillonite may be introduced in polymers/fibers, resulting in an increased resistance to electricity, chemicals, heat and flaming, and enhanced ability to block UV light.

Montmorillonite may be incorporated in fiber-forming polymer through electrospinning/melt spinning. Electrospinning is the technique successfully used for the production of a variety of polymer nanofibers.

The properties of polymer nanofiber produced through electrospinning are influenced by melt viscosity, surface tension, dielectric permeability, electric field strength, solvent properties to evaporate, polymer molecular weight, and concentration.

6.9. Flame-retardant finishing of cotton fiber

Interest in using the clay was observed to obtain the flame-retardant properties in cotton fiber [44]. The two types of local clay samples study to evaluate the flame-retardant effects on bleached cotton fabric.

Aqueous water dispersion was applied to bleached cotton fabric. The finished fabric was assessed using vertical flame-retardant test BS EN ISO 6940 2004. Flame retardancy was improved as indicated by the ease of ignition and the char length of burnt cotton fabric.

6.10. Geological repository for spent nuclear fuel

The growing variety of montmorillonite utilization is perhaps indicated by the use of bentonite in the study to form a part of deep geological repository for spent nuclear fuel. Pure homo ionic Ca-montmorillonite may be considered bentonite-similar system to obtain information on natural bentonite behavior. Water-saturated structure and porosity of Ca-montmorillonite were studied using X-ray diffraction, small angle X-ray scattering, nuclear magnetic resonance, transmission electron microscopy, and ion exclusion. The obtained results indicate multiple porosity for the bentonite structure [45].

Multiple porosity model supports two different groups of water present in bentonite: one present in the interlamellar space and the other found in the volume between clay stacks.

6.11. Bronsted acidity

Synthetic mica-montmorillonite (SMM) shows Bronsted acidity. SMM studied, for Bronsted acidity, was based on

- i. isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedral layer, and additional NiF doping,
- ii. the effects on platelets, and
- iii. the edge termination of clay platelets.

The evaluation of SMM for adsorption energies using ammonia and pyridine showed the acid strength. The composition of SMM platelets influences the acidity [46]. Interesting results were obtained in the study explaining the Bronsted acidity in relation to the platelet structure.

The strongest acidity was demonstrated by SMM structure where octahedral $[\text{AlO}]^+$ was replaced adjacent to tetrahedral $[\text{Si}(\text{OH})\text{-Al}]$ moieties in the tetrahedral layer.

Bronsted and Lewis acid catalytic sites in montmorillonite provided the useful applications [47]. The exchangeability of interlayer cations, through ion exchange, helps in altering the acidic nature. Modified montmorillonite types known as montmorillonite-K-10 (produced by the calcinations of montmorillonite) were found as efficient catalysts. Cation exchange produces more effective montmorillonite types including Fe^+ montmorillonite and clayfen.

Sodium montmorillonite (NaMMT) is indicated to accelerate the curing of urea-formaldehyde resin. In acid-curing conditions, urea-formaldehyde resin was used as adhesive for plywood and wood particleboard. Cross-linking of urea-formaldehyde in the presence of NaMMT produces plywood with improved water resistance. An accelerating effect on urea-formaldehyde curing was observed in differential scanning calorimetry results. Dry internal bond strength of wood particleboard increases with small additions of NaMMT [48].

Organic reagents synthesized using montmorillonite types (cation substituted) used as catalyst include α -aryl β -hydroxycyclic amines, silanols, and methyl cinamates, and the production of multi-substituted imidazopyridines, imidazopyrazines, and imidazopyrimidines.

7. Environment concern

Green chemistry is a demanding approach in organic synthesis, where the release of hazardous gases and liquids is undesired. Environment damage and ecological balance are required to be least affected. Montmorillonite is a solid acid used in organic synthesis. It has the potential to replace liquid acid catalyst with greener effects (**Figure 2**).

Natural and modified clays, including montmorillonite, received significant interest as catalyst (Section 7.8). The use of montmorillonite as a greener catalyst in organic synthesis is reviewed [49]. Several clay-based or montmorillonite-based catalysts are available in market including claycop TM, clayfen TM, clayzinc TM, envirocat TM, and so on.

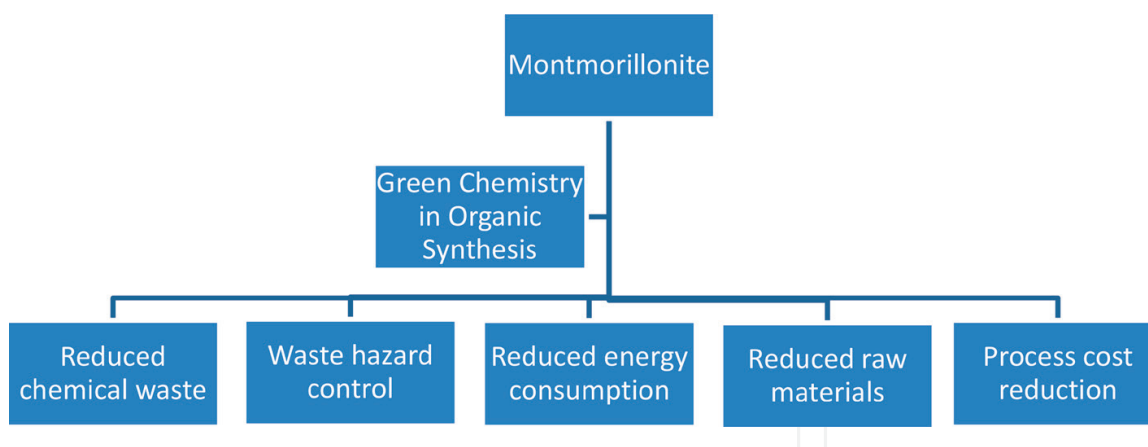


Figure 2. Green chemistry effects in organic synthesis using montmorillonite as catalyst.

Good mining practices have shown bentonite as environmentally not hazardous provided dust abatement mask used. Bentonites demonstrate good performance as sealant and absorbent and used as barrier for landfill and toxic waste repository.

Environmental concern in the extraction, use, and application of clay can range over the environmental characteristics of clay type and its minerals (=minerals present in clay sample). Montmorillonite particles, depending upon the size range, may come in contact with living species. The health and safety concern related to montmorillonite particles received interest for study.

The nature and distribution of inorganic contaminants, such as metals and metalloids like arsenic, iron, and lead, in clay-bearing rocks, may introduce the environmental concerns. These environmental factors may influence the use of clays in natural and industrial applications [50].

Information obtained on environmental effects for industrial minerals, including various clay types, sand, gravel, and crushed stone may not be applicable to montmorillonite composition, and studies will be more useful that is clearly based on any montmorillonite structure.

Information on occupational exposure to bentonite dust in mines, processing plants, and user safety is limited [5]. Varying amount of silica is present in bentonite and kaolin clays; however, there are no reported cases of marked diffuse/nodular pulmonary tissue fibrotic reaction to montmorillonite containing no free silica. Bentonite comprising montmorillonite as major fraction, and kaoline have not shown local or systematic adverse effects in cosmetics. However, these were indicated to cause reduced toxicity toward aquatic organisms.

Particle size and the chemical structure of montmorillonite are two obviously different aspects. The increased concerns in the toxicity of airborne fine (0.1–2.5 μm) and ultrafine (<0.1 μm) particles received research interest. Epidemiological studies indicated an increase in morbidity, and mortality was associated with the rise in airborne particles, particularly in ultrafine size range. The decreasing potencies of quartz, kaolinite, and montmorillonite to introduce lung damage were related to their known relative active surface areas and surface chemistry. Therefore, handling of ultrafine particles requires more vigilant control to abate health effects.

Natural clay particles are smaller than 0.004 mm in diameter; however, manufactured nanoclay particles are in ultrafine size range and have shown toxic properties [1]. These nanoparticles

can enter human body, reaching vital organs through blood circulation. The possibility is therefore indicated for tissue damage. Nanosized particles coming in contact with the tissue may introduce toxicity and health concerns; however, particles incorporated in the bulk materials or polymer products will not be exhibiting such effects.

Therefore, there is clear partition line in risk assessment for two types of particle composition: ultrafine, and agglomerated and bulk material. The properties of nanosized particles are different from the bulk material of the same composition.

Beneficial effects of montmorillonite are known in the form of a voluminous product used effectively and discussed in Section 7. Calcium montmorillonite is also known as “living clay” being containing minerals capable to improve enzyme production in living organisms [51, 52].

It is important that there are several standards practiced, mainly in industrialized regions, addressing the health and safety risks at work places. Therefore, it is unlikely that the future would eliminate montmorillonite uses.

8. Conclusion

Clay minerals have long been benefiting the human and society. Montmorillonite, an important clay type, has received growing interest in utilization as an additive in polymer and products for enhanced effects. Bentonite is an important source of montmorillonite in nature.

The basic molecular structure comprises silica tetrahedron and aluminum octahedral. The cation Si^{+4} is fourfold and possesses tetrahedral coordination with oxygen, while the cation Al^{+3} occurs in sixfold or octahedral coordination. Chemical composition, ionic substitution, layer structure, and particle size of natural clay minerals are important to introduce the functional properties and effects in the application of montmorillonite. Sheet structure was used to classify the clay minerals, and chemical composition was used for nomenclature.

Important applications of montmorillonite include uses additive for food, health, and stamina, for antibacterial activity, improved polymer performance; as sorbent for nonionic, anionic, and cationic dyes; and as green chemistry catalyst in organic synthesis, and so on.

Conflict of interest

The author declares no conflict of interest in publishing this chapter.

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