



Nanoclay and Its Importance

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Clays are the one of the most important minerals and have numerous applications in nanotechnology, helps in improve the product quality, cost effective and protect the environment from pollution. This review explained about the key characters of nanoclay particles and classification of nanoclay based on the sheets arrangements in their structural unit called layer. Nano clay major groups are kaoline-serpentine, smectite, mica, vermiculite, pyrophyllite talc and chlorite. The physico-chemical and morphological properties of halloystite and mantmorillonite clay represents the 1:1 and 2:1 layer groups respectively. Nano clays are the group which is naturally present in the soil fraction of clay and most important nano clay material present in the soil are montmorillonite and allophone. Montmorillonite is a characteristically crystalline, phyllosilicate and hydrous silicate layer. Organo clays are the organically modified forms of the montmorillonite and formed from quaternary ammonium ions intercalation process and which have been used in inks, rheomodifiers, cosmetics, greases, as a additives in paints and also used in controlled release of drugs in delivery systems. Largest usage of nanoclays being practiced in polymer-clay nanocomposites. Organo clays are most importantly using in water treatment and pollution control.

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Allophane is formed by weathering of volcanic ash; it is non crystalline aluminium silicate derivative. Agricultural lands in Chile mostly formed by the allophane clay fraction. It is most suitable for enzyme mobilization. It also very useful in abortion of phenolic compounds, mill effluent colours and phosphates from waste water.

Keywords: Allophane; montmorillonite; organoclays and phyllosilicate.

1. INTRODUCTION

The term 'nano' comes from the Greek nanos, meaning dwarf and when used as a prefix indicates 10^{-9} . A widely accepted definition for nanomaterials is that their particles have at least one dimension which is <100 nm [1]. Because of their nanoscale dimensions and large surface area/volume ratio, nanomaterials have properties (electronic, kinetic, magnetic, and optical) that are very different from those of their bulk counterparts. For example, nanomaterials are transparent, since their particles are smaller than the wavelength of light. We might add that some properties of nanoparticles may not be predictable due to the increased influence of superficial atoms or quantum effects [1]. Some nanomaterials (e.g. carbon black, soot) have long been known and used by humans. Humans are also exposed to a range of engineered and anthropogenic nanoparticles (e.g. carbon nanotubes, fullerenes, photocatalysts, vehicle exhaust emissions) in the ambient environment (air, water, soil), raising concerns about their potential adverse effects on health [2].

2. NATURAL NANOCLAY MATERIALS

Nanoclays are nanoparticles of layered mineral silicates. Depending on chemical composition and nanoparticle morphology, nanoclays are organized into several classes such as montmorillonite, bentonite, kaolinite, hectorite, and halloysite. Organically-modified nanoclays (organoclays) are an attractive class of hybrid organic-inorganic nanomaterials with potential uses in polymer nanocomposites, as rheological modifiers, gas absorbents and drug delivery carriers. Plate-like montmorillonite is the most common nanoclay used in materials applications. Montmorillonite consists of ~ 1 nm thick aluminosilicate layers surface-substituted with metal cations and stacked in ~ 10 μm -sized multilayer stacks. Depending on surface modification of the clay layers, montmorillonite can be dispersed in a polymer matrix to form polymer-clay nanocomposite. Within the nanocomposite individual nm-thick clay layers become fully separated to form plate-like nanoparticles with very high (nm \times μm) aspect

ratio. Sigma-Aldrich, in collaboration with the Nanocor Corporation, offers a range of montmorillonite nanoclay products with different organic modifications optimized to be compatible with various polymer systems.

Clay minerals are the basic constituents of clay raw materials and platy structure is the dominant morphology. Depending on the clay type, the individual layers could be composed of two, three or four sheets of either $[\text{SiO}_4]^{4-}$ tetrahedra or $[\text{AlO}_3(\text{OH})_3]^{6-}$ octahedra. The aluminosilicate layers organize themselves over one another like pages of a book, with a regular van der Waals gap between them, called an 'interlayer'. Interlayers possess net negative charge which is due to the ionic substitutions in the sheets of clay minerals. The layer charge is neutralized by cations which occupy the inter-lamellar. These inter-lamellae cations can be easily replaced by other cations or molecules as per required surface chemistry and hence called exchangeable cations. Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , are among common exchangeable cations present in the interlayer which are exchanged with other required cations. In general practice, to evaluate a material performance and its classification, chemical behavior is paid more importance. On the contrary to this general practice, the physical characteristics of clays are more important in defining various clay groups. Therefore, the clay minerals are broadly classified on the basis of the number and arrangement of sheets in a clay layer. Depending on the number and the way that the tetrahedral and octahedral sheets are packed into layers, the clay minerals can be classified into three classes, i.e., two-sheet layer, three-sheet layer and four-sheet layer [3].

3. STRUCTURAL AND PHYSICAL PROPERTIES OF NANOCLAYS

Nanoclays are fine-grained crystalline materials. A layer is the basic structural unit of nanoclays and these layers are prone to arrange themselves over one another like pages of a book. Individual layers are composed of the tetrahedral and/or octahedral sheets and this

arrangement of sheets plays a vital role in defining and distinguishing these clay minerals. In tetrahedral sheet, the silicon-oxygen tetrahedra are linked to neighboring tetrahedra by sharing three corners while the fourth corner of each tetrahedron forms a part to adjacent octahedral sheet. The octahedral sheet is usually composed of aluminum or magnesium in six-fold coordination with oxygen from the tetrahedral sheet and with hydroxyl. The sheets form a layer, and several layers may be joined in a clay crystallite. Vander Waals force, electrostatic force, or hydrogen bonding between the layers are the main drivers to clutch these layers with one another and form stacks of parallel lamellae. This stacking results in regular Van der Waal gaps between the adjacent layers. These spaces between the layers are called interlayer or gallery and can be accessed by water, organic cations or polar organic liquids. This intercalation weakens the forces clutching these layers with one another and causes the lattice to expand. The clay minerals' ability to accept changes in surface chemistry and delaminate into individual lamellae is their pertinent characteristics that have been widely exploited in the development of novel composites. The tetrahedral and octahedral sheets are building blocks for clay layers and these building blocks are capable of being assembled in a variety of arrangements. Thus the classification of nanoclay structure can be related to the arrangement of these building blocks; Clay minerals would have one tetrahedral

and one octahedral sheet; one octahedral sheet merged between the two tetrahedral sheets; and one octahedral sheet adjacent to one octahedral sheet merged between the two tetrahedral sheets per layer arrangements and are denoted as 1:1, 2:1 and 2:1:1 sheet arrangement. Examples of 1:1 sheet arrangement include kaolinite, halloysite and serpentine. The 2:1 phyllosilicates are comparatively larger group including Vermiculite, Pyrophyllite, mica etc. as sub groups. Among various expanding and non-expanding 2:1 phyllosilicate groups, smectites, strongly expanding 2:1 phyllosilicates also belong to this layer structure. The term smectite is used to represent a family of expansible 2:1 phyllosilicate silicate minerals having a general formula $(Ca, Na, H) (Al, Mg, Fe, Zn)_2 (Si, Al)_4 O_{10} (-OH)_2 \cdot xH_2O$, where x represents varying level of water attached to the mineral. Many well known natural and synthetic nanoclays viz., saponite, hectorite, montmorillonite, fluorohactite, and laponite belong to smectite family [3,4] [Fig. 1].

Halloysite: Halloysites were firstly discovered by Berthier as a clay mineral of the kaolin group in 1826, and were named "halloysite" after Omaliusd'Halloy who analyzed the mineral first time. These nanoclays are found worldwide and their deposits have been reported in countries such as Australia, China, Belgium, Brazil, France, Spain, New Zealand, Mexico, America and others [5,6]. Halloysites aluminosilicate sheets are rolled into tubes

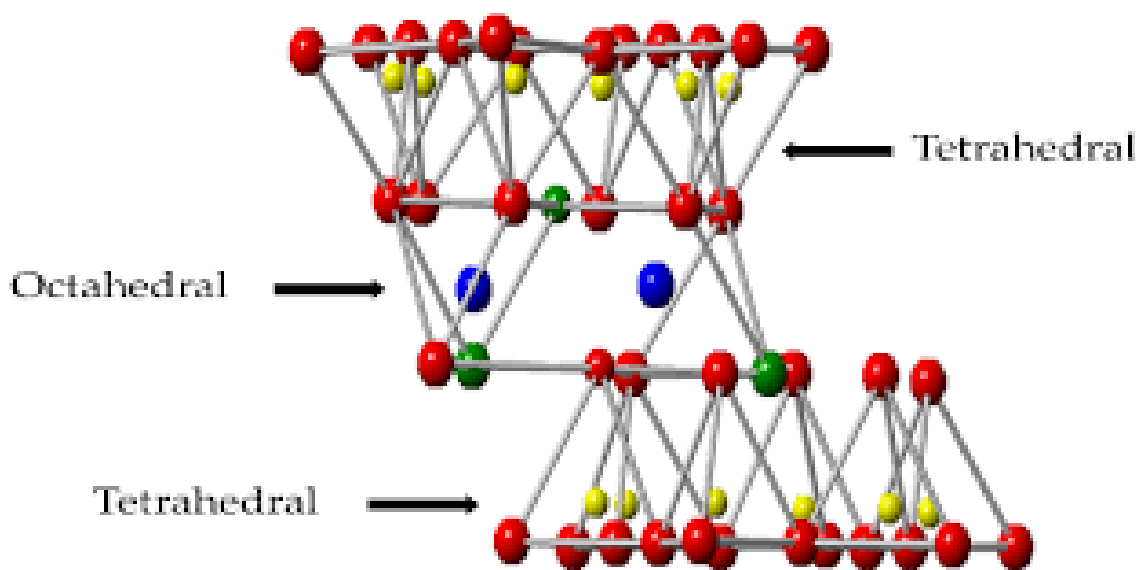


Fig. 1. General structure of nano clay

and nanosized tubular halloysite, also called halloysite nanotube (HNT) is morphologically similar to multiwalled carbon nanotubes (Figs. 2 and 3). Even though platy and spheroidal morphologies have also been reported in literature, the tubular structure is the dominant morphology of HNTs in nature and has attracted researchers from different scientific fields. HNTs are being used for long and the production of high-quality ceramics such as porcelain or crucible products have been among their traditional applications. However, with the recent advent of nanotechnology, these natural occurring materials with nano-scale lumens are being studied for a large range of new applications such as nano-containers for drug delivery, nano-templates for the fabrication of nanowires and nanoparticles, catalyst carriers, sorbents for contaminants and pollutants and nanofillers for polymers' reinforcement.

There is a layer of water molecules present between the halloysite multilayers ($n = 2$) and is called HNTs-10 Å (the "10 Å" designation indicates the d_{001} value of the layers). Dehydrated halloysite (HNT-7 Å when $n = 0$) or just commercial halloysite may be obtained through the loss of the interlayer water molecules under mild heating and/or a vacuum environment. It is worth noting that the dehydration of HNTs does not affect its morphology, however the removal of inter-layer water results in changes in lattice parameters.

Chemical composition of HNTs is same as platy clay kaolinite with water molecules and the unit layers in halloysites are separated by a monolayer of water molecules. Thus the interlayer water in HNTs is one of the main differences distinguishing halloysites from kaolinite. This interlayer water reduces the magnitude of electrostatic forces between adjacent layers of HNTs at the time of formation. Also, their differences in lattice parameters of alumina and silica in both a and b directions (for silica $a = 5.02$ Å, $b = 9.16$ Å, and for alumina $a = 5.07$ Å, $b = 8.66$ Å). These differences lead to dimensional mismatch of the sheets. In addition to lessen the electrostatic force between the adjacent layers, the presence of inter-layer water facilitates curvature of the layers to accommodate the dimensional mismatch of the octahedral and tetrahedral sheets. Consequently, halloysite crystallizes with the Al-OH sheet forming the inside and the Si-O sheet forming the outside of a unit layer [7,8].

Montmorillonite: Smectite nanoclays are among heavily researched nanofillers in the field of nanocomposites. Among these smectite nanoclays, montmorillonite (MMT) has got prominence over other member nanoclays owing to its abundance, environmentally friendliness and well-studied chemistry. MMT is dioctahedral nanoclay with the 2:1 layer linkage (Figs. 4, 5 and 6).

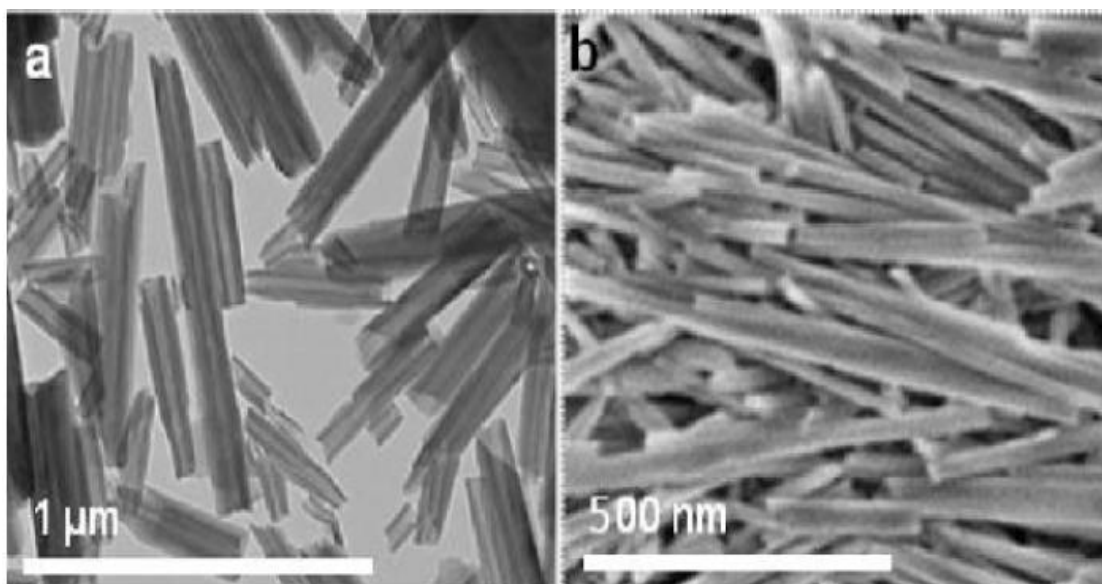


Fig. 2. TEM (a) and SEM (b) images of halloysite nanotubes

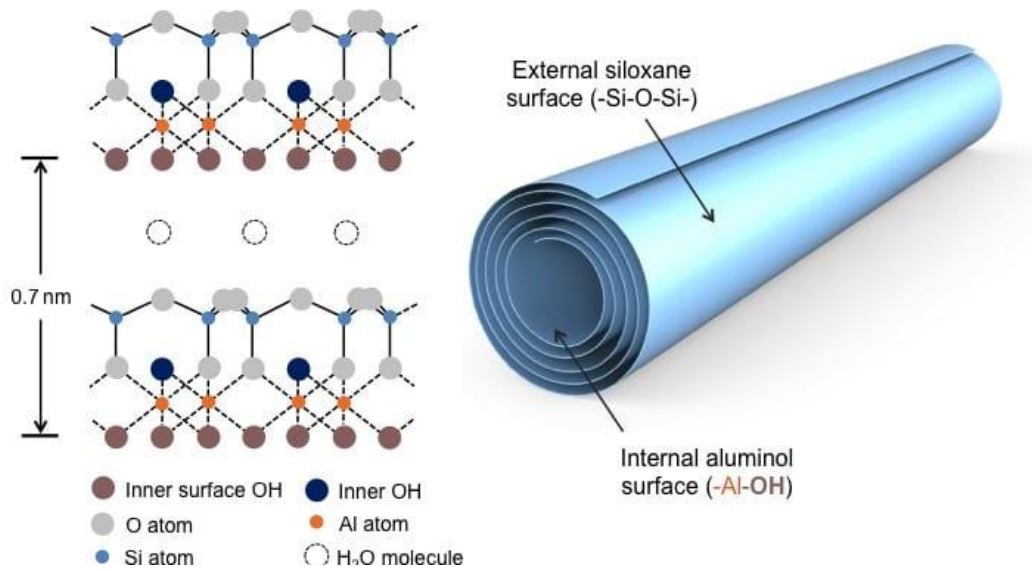


Fig. 3. Structure of hollisyite

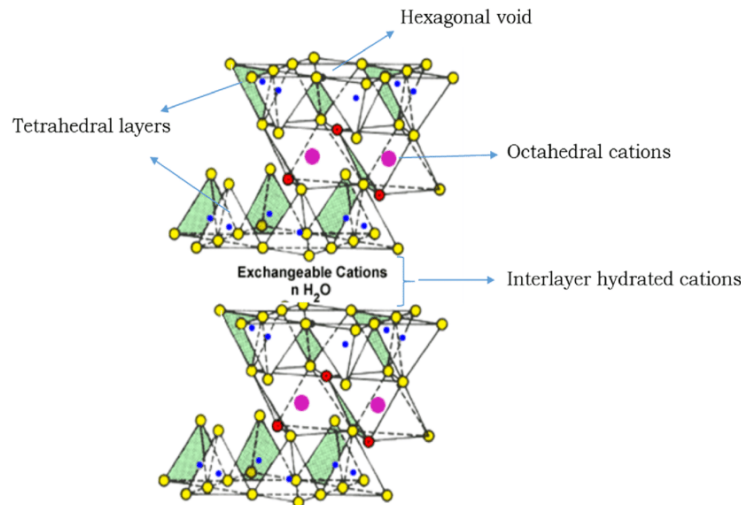


Fig. 4. Structure of montmorillonite

They are the most efficient reinforcement fillers and their reinforcing potential is well documented in literature. The studies revealed that larger surface area and large aspect ratio are the salient attributes responsible for the reinforcement [9,10]. Besides reinforcing effect of MMT, it is also viewed as rigid, impermeable filler. It creates a maze structure when dispersed in polymers, forces the moving gases/vapors to follow a tortuous path, and finally lowers their permeation rate. Each individual MMT layer having lateral dimensions of 200–600 nm and thickness of a few nanometers is composed of two tetrahedral sheets and an octahedral sheet.

The sheets are linked to each other in such a way that the silicon oxide tetrahedron (SiO_4) shares its 3 out of 4 oxygen atoms with the central octahedral sheets. MMT layers in its pristine form organize themselves over one another where the layered platelets are stacked with different levels of stacking within the clay mineral. Depending upon the stacking level, they could be primary particles or layered aggregates (micro-aggregates and aggregates). During the isomorphous substitution of Al^{+3} by Fe^{+2} or Mg^{+2} ; and Mg^{+2} by Li^{+1} in the layer structure, the difference in the valences induces an overall negative charge on each three sheets layer.

Different metal cations (Na^+ , Ca^{+2}) present between three sheets layers/in the galleries accommodate charge imbalance, thus increasing the hydrophilic behavior. Owing to this hydrophilic behavior, the hydration of MMT causes the galleries to expand and the clay to swell. In addition, the pristine clays are readily dispersed only in hydrophilic polymers (vinyl alcohol, ethylene oxide). To beaten this hydrophilic behavior and to make the clay compatible with hydrophobic polymers, the Na^+ present in the clay galleries can also be exchanged with organic cations, such as alkyl ammonium or alky phosphonium/onium ions. Murray [11] reported that the charge imbalance called as cation exchange capacity (CEC) in smectite is about 0.66 per unit cell due to the isomorphous substitution. The CEC depends on the nature of isomorphous substitutions and varies from layer to layer; hence an average value on the complete crystal is considered [12]. It is expressed as mequiv/100 g (meq/100 g) and is

reported to range from 80 to 150 mequiv/100 g for smectites [13].

Allophane: Allophane is a non-crystalline ('short-range order') aluminosilicate which, together with imogolite, which is present very widely in the soils which are derived from volcanic ash (Andisols). The unit of imogolite is tubular in structure and possess ~2 and 1 nm of inner and outer diameter respectively. Its formula is $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$, containing the Al/Si ratio of 2.0 it indicates the ions sequence towards tube periphery to the center where three oxygen particles are sharing with orthosilicate group (Fig 7 and 8). The hollow tube outer diameter is 3.5-5.0 nm. The wall of tube thickness is 0.7-1.0 nm and composed of Al octahedral sheet and an inner Silicon sheet. Allophane has highly specified surface area. The chemical properties of allophane-rich soils reflect the surface charge characteristic of this nanoclay.

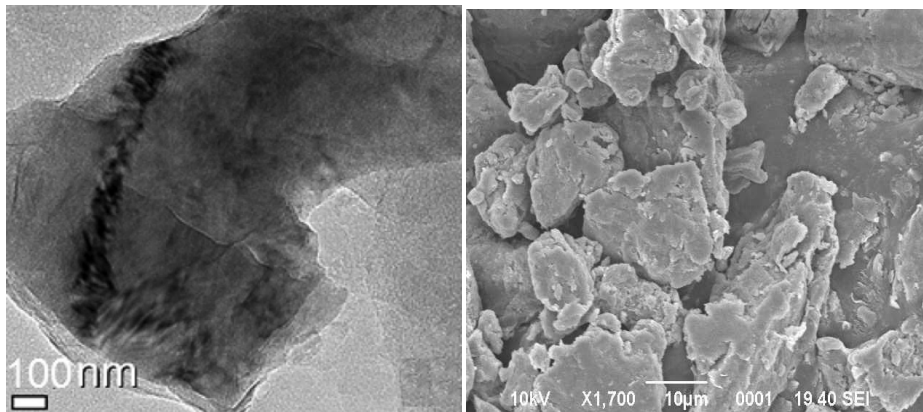


Fig. 5. TEM image of montmorillonite Fig. 6. SEM image of montmorillonite

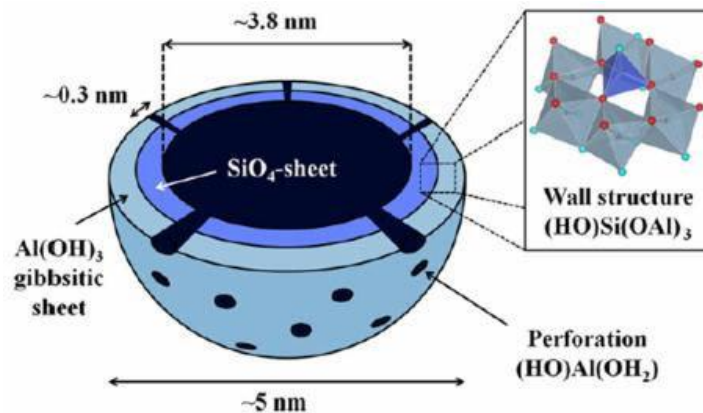


Fig. 7. Structure of allophane

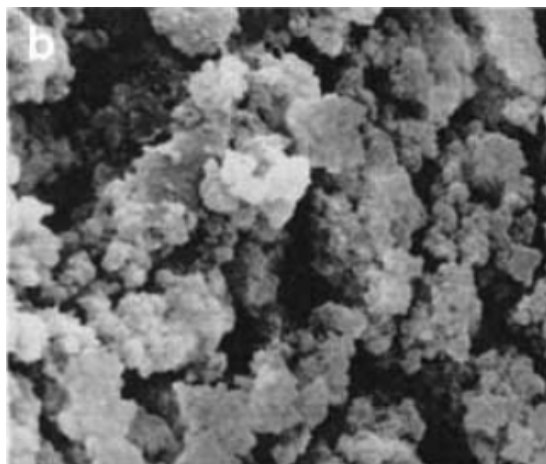


Fig. 8. SEM image of allophane

4. APPLICATIONS OF ALLOPHANE

The physical characteristics and fractal geometry of allophane aggregates are similar to those of synthetic mesoporous silica-based materials (e.g. MCM-41, MCM-48, SBA-15, HMS, MSU, MCF) showing a large surface area ($830\text{--}1500\text{ m}^2\text{ g}^{-1}$), large pore volume (1 ml g^{-1}) and well ordered pore structure (2–40 nm) [14]. Mesoporous silicas have found applications in biocatalysis and enzyme immobilization because they are stable at high temperatures, while their pore diameter matches the size of enzyme molecules [15]. Likewise, allophane would have potential applications in bio catalysis and enzyme immobilization. In keeping with this expectation, preliminary studies by our research group indicate that natural nanomaterials can serve as supports in enzyme immobilization. For example, acid phosphatase immobilized on an allophonic clay fraction from soil is 33% more active than the free enzyme [16]. This and similar findings with enzymes immobilized on different nanomaterials [17,15] have led us to develop suitable methods for extracting allophane from Chilean Andisols and explore its practical applications (Table 1).

Applications of nanoclay: Nanoclay composites are used in a number of novel applications, such as in asphalt mixtures, where they improve the rutting and fatigue resistance of asphalt mixtures, and enhance the storage stability and the aging resistance of polymer-modified asphalt mixtures Yang et al., [27]. Guo et al., [28] applied nanoclay assisted by surfactants as a stabilizer in CO₂ foam; according to the results, nanoclay improved the

stability and formability of CO₂ foam, which led to improved oil recovery from a homogeneous porous medium in a microfluidic device. The success of the implementation of surfactant/nanoclay composites as a foam stabilizer points to the petroleum industry and enhanced oil recovery as potential areas of application for these composites. Pierchala et al., [29] developed an antibacterial, multilayered poly(lactic acid)/halloysite nanoclay composite membrane encapsulated with gentamicin. A significant enhancement of the membrane's thermal stability and mechanical properties was observed after the incorporation of halloysite nanoclays. The synthesized composite membrane contained porous structures, which indicated its potential use in bone regeneration applications. Yahiaoui et al., [30] developed an antimicrobial food packaging material using poly (ε-caprolactone) (PCL)/nanoclay composites with mainly intercalated structures.

It inhibited about 90% of the growth of *Escherichia coli* and *Staphylococcus aureus*, and significant reduced water vapor permeability (WVP) values up to 56%. Ebrahimi et al., [31] investigated the effect of a PE/closite 20 nanoclay composite film on the quality-related parameters of mature peaches. The film had a selectable barrier property that allowed fruit respiration and inhibited bacterial growth. Peaches protected by the film exhibited lower polyphenol oxidase and higher peroxidase and catalase activities than the others. Pierchala et al., [29] developed an antibacterial, multilayered poly(lactic acid)/halloysite nanoclay composite membrane encapsulated with gentamicin. A significant

Table 1. Applications of allophane

S.No.	Applications	Author
1.	Acid phosphatase immobilization	Rosas et al., 2008 [16]
2.	Combined application of allophane and alkaline materials like calcite and dolomite is effective for stabilization of heavy metals in contaminated soils.	Isoyama and Wada, 2007 [18]
3	Suspension of allophane-rich material for water treatment to remove algae, suspended particles, and phosphorus.	Wada et al., 2008 [19]
4	Allophane used for automatic control of room humidity.	Shibasaki et al., 2000[20].
5	Soil organic matter (or carbon) is stabilized in soil through interactions with the smallest mineral particles, of which allophane and imogolite are the most effective members.	Percival et al., 2000 [21]
6	Allophane mineral containing Andisols were containing more organic matter than the inceptisols.	Parfitt et al., 1997 [22]
7	Natural and modified nanomaterials such as allophane and surface-modified smectite have high sorption distribution coefficients for Cu ions and naphthalene, and a high capacity to remove 17 β -estradiol from solution, suggesting that nanomaterials are effective sorbents for heavy metals, polycyclic aromatic hydrocarbons, and endocrine-disrupting chemicals.	Guodong Yuan, 2004 [23]
8	The sorption of humic acid by an allophanic clay in the presence of either NaCl or CaCl ₂	Yuvan et al., 2002[24]
9	Allophane nanoclay is a natural, inexpensive, and environmental friendly material suitable for removing phosphorus from water and waste water.	Guodong et al., 2007 [25]
10	allophanic soils do not usually have continuous macropores, they are excellent filters, capable of removing faecal coliforms and bacteriophages from effluents	McLeod et al., 2008 [26]

enhancement of the membrane's thermal stability and mechanical properties was observed after the incorporation of halloysite nanoclays. The synthesized composite membrane contained porous structures, which indicated its potential use in bone regeneration applications. Noori et al., [32] developed a smart composite hydrogel for wound dressing using polyvinyl alcohol/chitosan/honey/clay. The exfoliated nanoclay helped improve the swelling properties and honey-releasing rate of the material. The hydrogel exhibited more than 99% antibacterial activity.

The contamination of water due to the presence of an extensive variety of toxic substances, such as heavy metals, aromatic molecules, and dyes, has become a critical problem due to potential health concerns [33]. Adsorption is a widely used technique for the removal of

pollutants from water; a number of novel adsorbents have been developed in recent years [34]. Polymer/nanoclay composites are able to deliver a high adsorption capacity and an excellent life cycle for water treatment/remediation due to their easy processability, effective cation exchange, large surface area, and their relatively low cost and toxicity [35]. Kara et al., [36] fabricated poly(vinylimidazole) (PVI)/sepiolite nanoclay composites using an in-situ polymerization method. The synthesized composite was shown to be an effective adsorbent for Hg(II) in wastewater. PVI/sepiolite composites exhibited a dense, smooth surface and a uniform dispersion of nanoclay in the polymer matrix, which delivered a higher adsorption capacity compared to sepiolite alone. The optimum pH value for Hg(II) adsorption was observed to occur at a pH of six, whereas its adsorption capacity values

increased with the temperature. Yildiz et al., [37] employed PVI/bentonite nanoclay composites in wastewater treatment to remove anionic dye remazol black B (RB) from water. The maximum adsorption (230 mg/g) was achieved at a pH of two. Liu et al., [38] synthesized PANI/bentonite nanoclay composites by plasma-induced polymerization to remove radioactive uranium(VI) ions from aqueous solutions. Temperature, pH and ionic strength had significant effects on adsorption of uranium(VI) on PANI/bentonite surfaces. The adsorption capability of the PANI/bentonite was significantly enhanced within the presence of humic acid (pH < 6.5). El-Korashy et al., [39] reported the development of thiourea-formaldehyde/bentonite nanoclay composites for Pb(II), Mn(VII) and Cr(VI) adsorption in aqueous solution. The optimum pH was approximately four for Pb(II) and Mn(VII), two for Cr(VI). The maximum adsorption values were 13.38, 14.81 and 4.20 mg/g for Pb(II), Mn(VII) and Cr(VI), respectively. Regeneration experiments indicated removal efficiencies over 90% after four successive adsorption/ desorption cycles.

5. CONCLUSION AND FUTURE PERSPECTIVE

The study of nanoclays is a large field and shows an immense potential to be explored. Nanoclays have long been used in several applications and their uses are based on their structural and physical characteristics that are discussed in detail in this chapter. Introduction of nanoclays as fillers or additives in polymers for various desired effects has been of enormous interest for research and development studies. An interesting concern, along with the studies addressing how nanoclays change the behavior of polymeric materials, is to discover more about nanoclays. Various techniques that are used to characterize nanoclays are described in detail in this chapter and further studies could pay more attention to deep analysis with new advanced techniques. Despite clay minerals are ubiquitous in nature, several interesting nanoclays are not available in sufficient quantities therefore their synthesis will be a highlighted field of clay science and may lead to a breakthrough in the field of nanocomposites. Finding new applications of such synthetic clay minerals, including pillared clay minerals, porous clay hetero-structures, and nanocomposites, will be another promising work. Information on occupational exposure to nanoclays during extraction, development, and application is

limited and is highly desirable. An additional demanding area is the potential of nanoparticles (from packaging material) to migrate to packaged food and their eventual toxicological effects, if any.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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