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Modified nano-clay formulation and their application

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Abstract
Clay is a naturally occurring material composed primarily of fine grained minerals, which shows plasticity through a variable range of water content and which can be hardened when dried. Clay deposits are mostly composed of clay mineral (phyllosilicate mineral) and variable amount of water trapped in the minerals There are four main groups of clays i.e. Kaolinite, Montmorillonite (nano clay raw materials), illite and chlorite (Faheem uddin, 2008). Nano clay are minerals which have a high aspect ratio and with at least one dimension of the particle in the nanometer range.Impurities act as stress concentrators, resulting in poor impact and tensile properties (M. S. Nazir *et al.,* 2016). Nano-clay polymer composite are potential agro-biotechnological applications for increase in input use efficiency especially fertilizer and water under abiotic stress condition. Improves water holding capacities and Nutrient release behaviour of nutrients (Raj Mukhopadhyay *et al.,* 2014). Nano-clay finds various applications like treatment of improving soil health, drug delivery system etc. Application of nano fertilizers will drastically bring down the use of chemical fertilizer with improvement in the crop yield. Nano fertilizers will also improve the soil aggregation; moisture retention and carbon build up of the soil. The use of nanomaterials for delivery of pesticides and fertilizers is expected to reduce the dosage and ensure controlled slow delivery. Modification of clay particles with nanomaterials reduces the toxicity of soil by removing pollutants and heavy metals and thus its effects entering the food chain can be reduced.

Keywords: Clay, Nano-clay

Introduction
The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried. Clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried. Associated phases in clay may include materials that not impart plasticity and organic matter.
Clay belongs to a wider group of minerals; however, in chemistry, all clay minerals may simply be described as hydrous silicates. In terms of their natural locations, clay minerals can be divided into two classes: residual clay and transported clay (or sedimentary clay).Residual clays are produced from the surface weathering of rock or shale (a dark fine-grained sedimentary rock composed of layers of compressed clay, silt, or mud) through various means, and they are generally found in the place of origin. Residual clays could be produced by the chemical decomposition of rocks, i.e., granite containing silica and alumina; by the solution of rocks, i.e., limestone; and by the disintegration and solution of shale. The transported clay, the second type, is removed from the original deposit through erosion and deposited to a distant place (Faheem uddin, 2008) [5].

Importance of clay minerals
- Clay contributes many benefits to the physical, chemical and biological properties of soil.
- It increases the soil's cation exchange capacity, enhances water holding capacity, provides elasticity, acts as a binding agent for the non-clay components, and reduces nutrient loss through leaching.
- The buffering capacity of soil is enhanced by clay, which means that growers do not have to apply lime as often.
- Clay is an essential component of a productive soil.
- It plays a vital role in holding plant nutrients and water.

Nano-clay

Nano-clay composed of thin layers; each layer has a thickness of one to a few nanometers length from a few hundred to several thousand nanometers. Nanoparticles used as fillers or additives in polymers for various desired effects are receiving an increased interest for research and development. Various types of nanoparticles, including nanocarbon, carbon nanotubes, nano-clays, and metal oxides, are currently used to modify the polymer performance. The viable interest in the use of nano-clays for the modification of polymeric material for numerous applications may be indicated from the increased commercial interest, and consumption of clay nano-composites that was almost one-quarter (24 pct) in 2005 of the total nano-composite consumed (McWilliams *et al.,* 2006) [2]. Moreover, the nano-clay composites are estimated to raise their market share to 44 pct by 2011. Apart from the studies addressing how nano-clays and montmorillonite change the behaviour of polymeric material, an interesting concern is to know what these nano-clays and clays consist of. The purpose of this study is to discover clay minerals with particulars reference to nano-clays and montmorillonite minerals.

Physical parameters of nano-clay

- Molecular mass (g / mole) 540.46
- Average weight (g / cm^3) 2.35
- Monoclinic crystals
- Colour white, yellow

Variable nano-clay

Nano-clay is an inorganic, hydrophilic. While the polymer matrix used to make nano-composite materials is organic and often hydrophobic. Therefore, nanoclay is very difficult to mix with polymer. In order to increase the compatibility between the nanoclay and the polymer, the nano-clay must be modified. There are several methods (techniques) used to denote the nano-clay, in which the most commonly used method is ion exchange.

Ion exchange method

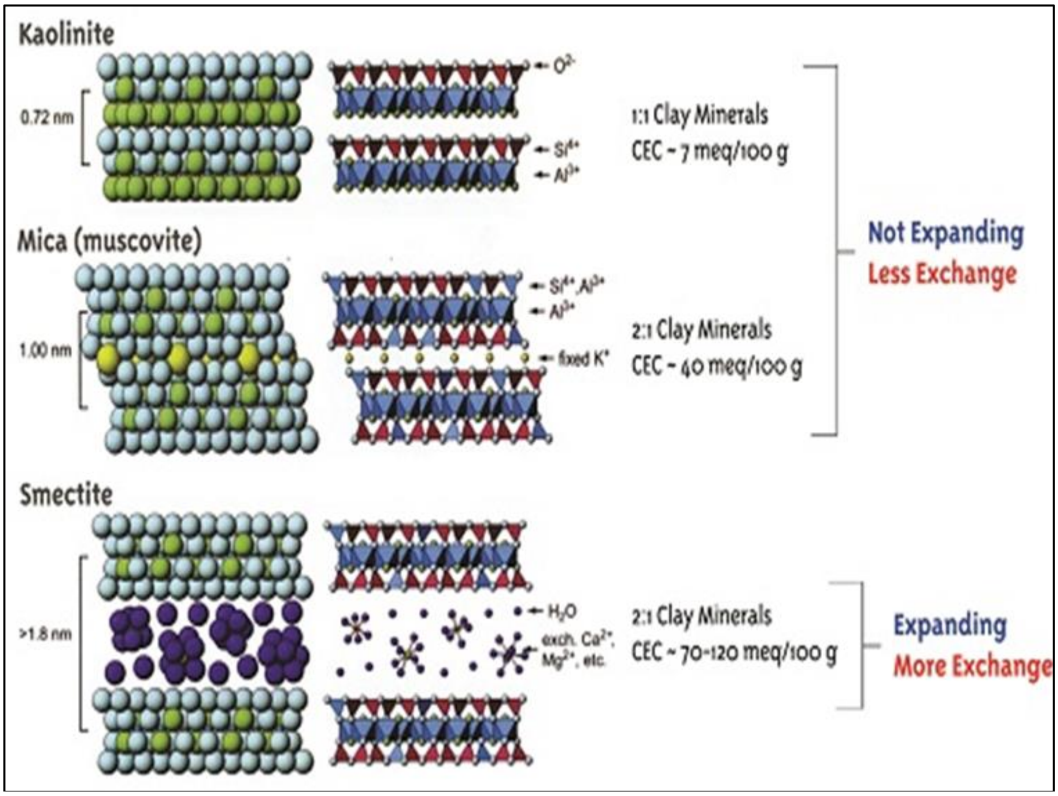
As mentioned above, the link force between the clay layers is the link force Van der Waals. This is a type of physical linking force, which has very small binding energies. So the bonding of clay layers together is very poor, so other molecules can interlace between the clay layers quite easily. To make MMT becomes hydrophobic, good compatibility with the polymer, the cations in between layers of clay are replaced by the surfactant cations such as alkyl ammonium or alkyl phosphate. When denatured by cationic surfactants, the positive electrode is directed towards the clay surface (due to the electro-negativity interaction) and the alkyl rings point outward. Here we are interested in a quantity used quite a lot when investigating cation exchange is the CEC (cation exchange capacity) of the clay. It is the largest number of cations that can be exchanged, which is constant for each specific type of lightning. It is calculated in milliard equivalents for 1 gram (meq / g) or more commonly the equivalent millimeter for 100 grams (meq / 100 grams. The cation exchange capacity of montmorillonite ranges from 80 to 150 meq / g. After modifying organic matter, the clay surface becomes partially hydrophobic, its surface energy decreases so it is compatible with organic polymers. The larger the size of the alkyl group, the higher is the hydrophobicity of the clay and the spacing between the nano-clay layers. The arrangement of the alkyl circuit between the clay layers depends on two factors: the charge density of the clay and the type of surfactant. The longer the length of alkyl,the greater the density of lightning, the greater the distance (M. S. Nazir *et al.,* 2016) [13].

Structural and Physical Properties of Nano-clays

Nano-clays are fine-grained crystalline materials. A layer is the basic structural unit of nano-clays 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 neighbouring 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 aluminium 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 are 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 nano-clay 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 $(Ca, Na, H) (Al, Mg, Fe, Zn)_2 (Si\ Al)_4O_{10}(\text{-}OH)_{2\text{-}x}H_2O$, where x represents varying level of water attached to the mineral. Many well-known natural and synthetic nano-clays viz. saponite, hectorite, montmorillonite, fluorohactite, and laponite belong to smectite family (Floody *et al.* 2009; Lee and Tiwari 2012) [4, 12]. It is worth noting that despite sheet arrangement similarity of the member clays of a particular clay group, the lateral dimensions of all the members are different. In addition, the layer dimensions vary not only for each member clay, but also for the same clay from different origins. Depending upon the number of factors, including source of clay, method of preparation and particulate clay, the thickness of each layer is about 1 nm with lateral dimensions ranging from 300 Å to several microns (Lee and Tiwari 2012; Pavlidou and Papaspyrides, 2008) [12, 14].

Structure of clay minerals



Kaolinite

Kaolinite is a 1:1 non-expanding type of mineral. Si_4 Al_4 $O_{10}(OH)_8$. Platy shape The bonding between layers are van der Waals forces and hydrogen bonds (strong bonding).There is no interlayer swelling Width: 0.1~ 4μm, Thickness: 0.05~2 μm. Kaolinite has a low shrink–swell capacity and a low cation-exchange capacity (1–15 meq/100 g). It is a soft, earthy, usually white, mineral (dioctahedral phyllosilicate clay), produced by the chemical weathering of aluminium silicate minerals like feldspar. In many parts of the world it is colour pink-orange-red by iron oxide, giving it a distinct rust hue. Lighter concentrations yield white, yellow, or light orange colours.

Mica

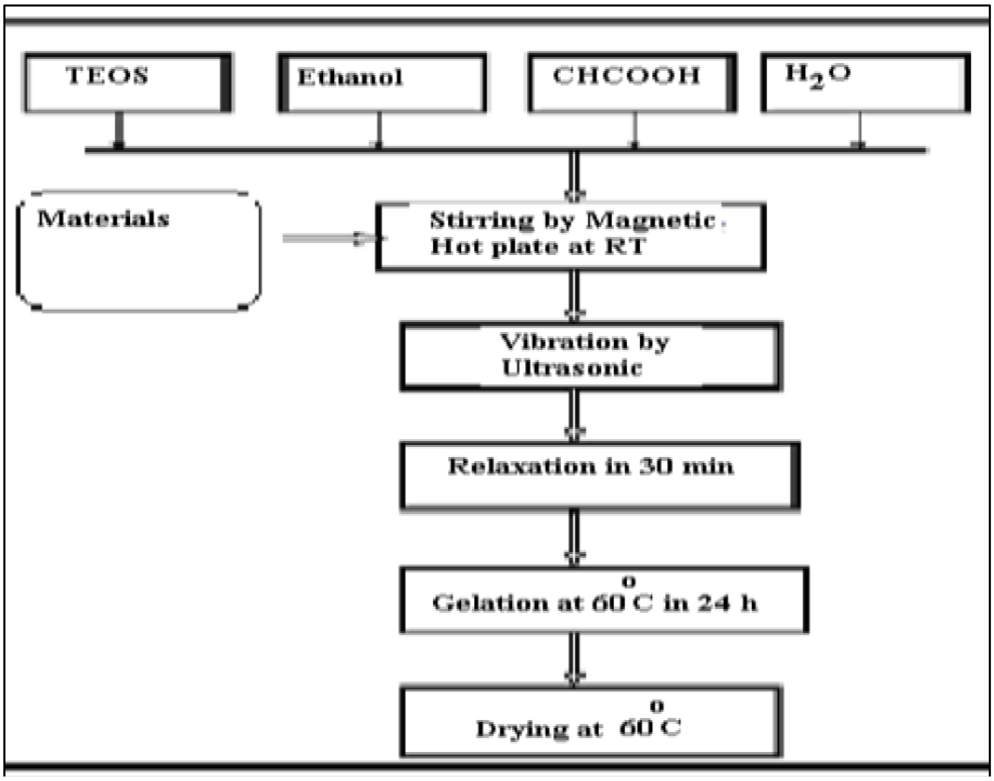
2:1non-expanding type of clay minerals. $Si_8(Al, Mg, Fe)_{4\sim6}O_{20}(OH)_4\cdot(K,H_2O)_2$. Flake shape. The basic structure is very similar to the mica, so it is sometimes referred to as hydrous mica. Illite is the chief constituent in many shales. Some of the Si^{4+} in the tetrahedral sheet are replaced by the Al^{3+}, and some of the Al^{3+} in the octahedral sheet are substituted by the Mg^{2+} or Fe^{3+}. Those are the origins of charge deficiencies. The charge deficiency is balanced by the potassium ion between layers. Note that the potassium atom can exactly fit into the hexagonal hole in the tetrahedral sheet and form a strong interlayer bonding. The basal spacing is fixed at 10 Å in the presence of polar liquids (no interlayer swelling).

Smectite group of clay minerals

Smectite group of clay minerals are montmorillonite, saponite and hectorite the are used for preparation of nano-clay. The clays used for the preparation of nano-clays belong to smectite group clays which are also known as 2 :1 phyllosilicates, the most common of which are montmorillonite $\{Si_4[Al_{1.67}Mg_{0.33}]O_{10}(OH)_2.nH2O.X_{0.33}$ = Na, K or Ca} and hectorite $\{Si_4[Mg_{2.7}Li_{0.3]}O_{10}(OH)_2.X_{0.4}$ = Na}, where octahedral site is isomorphically substituted. Other smectite group clays are beidillite $\{[Si_{3.67}Al_{0.33}]$ Al_2 O_{10} $(OH)_2.nH_2O$. $X_{0.33}$ = Na, K or Ca}, nontronite $\{[Si_{3.67}Al_{0.33}]$ Fe_2O_{10} $(OH)_2$. $X_{0.33}$ = Na, K or Ca} and saponite $\{[Si_{3.67}Al_{0.33}]$ Mg_3 $O_{10}(OH)_2.X_{0.33}$ = Na, K or Ca} in which tetrahedral site is isomorphically substituted. Crystal lattice of smectite group clay consists of a two-dimensional, 1 nm thick layers which are made up of two tetrahedral sheets of silica (SiO_2) fused to an edge-shaped octahedral sheet of alumina. The purity of the clay can affect the final nano-composite properties; due to this it is very important to have montmorillonite with minimum impurities of crystalline silica (quartz), amorphous silica, calcite, kaolin etc. The technique mainly used for purification of clays includes hydrocyclone, centrifugation, sedimentation method and chemical treatment (Jasra *et al.*, 1995) [8]. Clays are inexpensive materials, which can be modified by ion exchange, metal/ metal complex impregnation, pillaring and acid treatment to develop catalysts with desired functionality (Taqui Khan *et al.*, 1991; Halligudi *et al.*, 1992).

Hectorite is a clay mineral similar in structure to MMT but with more negative charges on its surface. It is also hydrophilic swelling clay composed of silicate sheets which delaminate in water to provide an open three dimensional structure.

Preparation of Nano Clay



The sol-gel process is a wet-chemical technique (chemical solution deposition) and/ or a bottom – up procedure, widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for an integrated network (or gel) of either discrete particles or network nano composites. Typical precursors are acetic, nitric, chloride, formic and sulphuric acids, which undergo various forms of reactions.

Thus, the sol evolves towards the formation of a gel-like diphase system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous networks. In this process, sodium clay powders (1.16 g) are dissolved in de-ionized water to which is added citric acid (0.38 g). The mixture is then stirred carefully using a magnetic stirrer while ammonium hydroxide is added to obtain a pH of 7. The mixture is then heated in a furnace to a temperature of 100°C for 20 h. Initially a zero gel and finally a powder are obtained.

Characterization

Characterization of nanomaterials and nanostructures has been largely based on the surface analysis techniques and conventional characterization methods developed for bulk materials. For example, X-ray diffraction XRD has been widely used for the determination of crystallinity, crystal structure and lattice constant nanoparticles, nanowires and thin films. The most straight forward tool is XRD because it is a good way to evaluate the spacing between the clay layers. XRD is one of best method of determining the structural and dispersion characteristics of nanoclay in polymers. It has been shown that this technique can be used to observe how layered nanoparticles are distributed in a polymer and characterize their degree of dispersion. Three distinct morphologies are possible when nanoclay is dispersed into epoxy resin, they are phase separated, intercalated and exfoliated (A. Bahari *et al.*, 2012) [1]

Types of nano-composite

Intercalated Nano Composites: The intercalated nano composites result from the penetration of polymers chains into the interlayer region of the clay, resulting in an ordered multiple layer structure with alternating polymer/inorganic layers at a repeated distance of a few nanometers.

Exfoliated Nano composites: The exfoliated nano composites involve extensive polymer penetration, with the clay layers delaminated and randomly dispersed in the polymer matrix. Exfoliated nano-composites have been reported to exhibit the best properties due to the optimal interaction between clay and polymer.

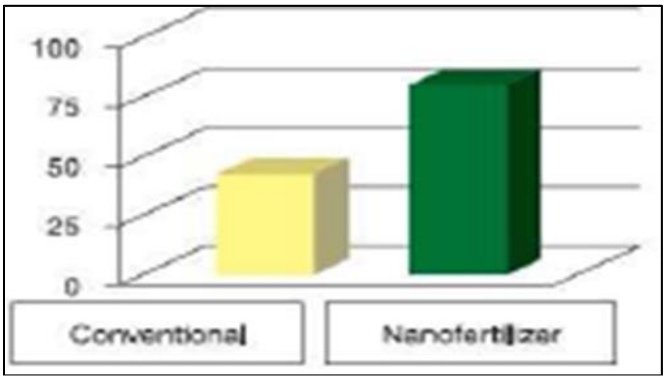
Applications of nano-clay

Nano-clay composite and phyto-nanotechnology: a new horizon to food security issue in Indian agriculture

Jahnavi *et al.*, 2015 [7] studied the in this article different and unique utilization of nano-clay polymer composite and Phyto-nanotechnology, to achieve the goal of food and nutritional security and safety in India. These emerging technologies can be proved as powerful candidates for enhancing nutrient use efficiency, upgrading activity and efficacy of bioagents and PGRs and regulating use of agrochemicals in field. In a nut shell, how these nano-integrated strategies would obviously strengthen the backbone of rainfed agriculture that occupied significant cropped area and how would tide over the hurdles of climate change and promote the productivity issue in Indian agriculture is described here. The other aspect of this article is to portray the processes of green or organo-manufacturing of NP and NMs by Phyto-nanotechnology and clay polymer composites. Because this benign approaches not only will diminishes the risks of eco toxicity but also opens up enormous scope for employing nanotechnology in Indian agriculture.

They also studied in this article Nano-clay –hybrid: A useful smart delivery system:

The world demand for fertilizer consumption is increasing day by day where as its use efficiency is declining. The nano-clay loaded with different fertilizer like N, P and K show the slow release due to intercalation of clay surrounding the polymer composite. In India, Bansiwal *et al.* (2006) [3] developed a surface modified zeolite as a carrier of slow release phosphatic fertilizer. Liu *et al*. (2006) [3] have shown that nano-composites containing organic polymer intercalated in the layers of kaolinite clays can be used as a cementing materials to regulate the release of nutrients from conventional fertilizers. Nano-fertilizers are capable of releasing nutrients, especially NO3-N for more than 50 days as compared to conventional fertilizer (urea) which ceased to exist beyond 10-12 days (Subramanian and Rahale, 2000) [15]. The properties of nano-particles (more surface area) may help in increasing the reactive points of these particles and hence increase the reactivity of these nanoparticles.



Nitrogen-use efficiency (%) of conventional and nano-fertilizer

Nano-clay encapsulation of bioagents and PGRs are excellent vehicle for plant protection

Reported that there was a clear distribution of conidia of *Trichoderma hazarium* UPM40 loaded in Ca-alginate MMT clay. Nano clay coated bioagents can retain their activity for longer period as well as can serve other nutritional supplementation too. The NCPC loaded *Trichoderma sp*. or *Pseudomonas sp* can control several fungal nematode disease complex that occur in pulses due to moisture and nutrient deficiency in rainfed rabi crops.

Applications of NCPC are in Agriculture

- Potential agro-biotechnological applications for increase in input use efficiency especially fertilizer and water under abiotic stress condition.
- The slow release pattern of nutrients are potentially helpful to control the deficiency of major nutrient elements in soils like N,P,K *etc* in the eastern part of India.
- Improves water holding capacities and Nutrient release behaviour of nutrients.
- Enhance water absorption and retention properties of sandy loam soil.
- Encapsulation of different bioagents like *Trichoderma harzianum*, *Pseudomonas fluorescens through NCPC can control fungal-nematode disease complex that occurs in* several pulses due to moisture and nutrient deficiency causing low level of productivity in rainfed rabi cropping.
- NCPC loaded with biological control agents like *Trichoderma harzianum coupled with nutrient elements can go a long way for* promotion of a second crop after rice in rainfed ecosystem.

General Applications

Organoclay is used in the ink formulation: It helps to adjust the consistency of printing inks to the desired value, avoiding pigment sedimentation, providing good colour distribution, obtaining desired film thickness, etc. by incorporation of small amount of organically modified layered silicate.

Thickening lubricating oils with organoclays can produce specially high temperature resistant lubricating greases. Organoclay also gives good working stability and water resistance to the greases. Such greases are typically used for lubrication in foundries, mills and on high-speed conveyors, agriculture, automotive and mining (Somani *et al* 1999) [16].

The performance of cosmetics is enhanced by the use of organoclays and they allow good colour retention and coverage for nail lacquers, lipsticks and eye shadows. They have been tested to be non-irritant for both skin and eye contact (Tatum and Wright 1988) [18].

Nano-clay as drug vehicle

The continuous development of new controlled drug delivery systems is driven by the need to maximize therapeutic activity while minimizing negative side effects. One class of drug delivery vehicle that has received more attention in recent years is layered materials which can accommodate polar organic compounds between their layers and form a variety of intercalated compounds. Because the release of drugs in drug-intercalated layered materials is potentially controllable, these new materials have a great potential as a delivery host in the pharmaceutical field. Calcium montmorillonite has also been used extensively in the treatment of pain, open wounds, colitis, diarrhea, hemorrhoids, stomach ulcers, intestinal problems, acne, anemia, and a variety of other health issues. Not only does montmorillonite cure minor problems such as diarrhea and constipation through local application, it also acts on all organs as well (Lee and Fu 2003; Lee and Chen 2004) [10].

In addition to surface unmodified and modified montmorillonite, layered double hydroxides are also used as drug carrier in various applications. Intercalation of fenbufen in a layered double hydroxide followed by coating with Eudragit® S 100 gives a composite material which shows controlled release of the drug under *in vitro* conditions which model the passage of a material through the gastrointestinal tract (Sheng-Ping 2005) [19]. Intercalations of anti-inflammatory drug in layered double hydroxide have the advantage of gradual release over a longer period of time. Gene therapy is gaining growing attention for the treatment of genetic deficiencies and life-threatening diseases. For the efficient introduction of foreign DNA into cells, a carrier system is required. Recently, it has been successfully demonstrated that novel layered double hydroxide could form a nanohybrid by intercalating with bimolecular anion such as mononucleotides, DNA which shows that antisense oligo nucleotide molecules packaged in the layered double hydroxide can enter cells, presumably through phagocytosis or endocytosis. The leukemia cells were used to explore the layered double hydroxide's potential as gene carriers (Seo-Young *et al* 2002) [17].

Wastewater treatment

The use of organoclays in wastewater treatment has become common in industry today. Organoclays exhibit a synergistic effect with many commonly utilized water treatment unit processes including granular-activated charcoal, reverse

osmosis, and air strippers. Granular-activated carbon is particularly effective at removing a large range of organic molecules from water, however, is very poor for removing large molecules such as humic acid and wastewaters containing emulsified oil and grease. Organoclays have proven to be the technology of choice for treating oily wastewaters (Jasra *et al* 1995) [8].
Humic acid is one of the common contaminant in potable water and is difficult to remove with conventional flocculation techniques commonly used for drinking water treatment and activated carbon is very ineffective due to its weak interaction with humic acid.The comparative studies for removal efficiencies of humic acid from ground water using different sorbents.

Future perspective

- Despite clay minerals are ubiquitous in nature, several nano clays are not available in sufficient quantities therefore their synthesis will be highlighted in the field of clay science and may lead to a breakthrough in the field of nanocomopsites
- Information on occupational exposure to nano clays during extraction, development and application is limited and is highly desirable.
- Finding new application of such synthetic clay minerals and nanocomposites will be another promising work.

Conclusions

- The use of nanomaterials for delivery of pesticides and fertilizers is expected to reduce the dosage and ensure controlled slow delivery.
- Sol–gel method can be used for synthesis of nano clay using ethanol and some acids as organic solvents.
- Modification of clay particles with nanomaterials reduces the toxicity of soil by removing pollutants and heavy metals and thus its effects entering the food chain can be reduced.

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