RESEARCH PAPER

Nanoclays: Structure, Functionalization, Applications, and Future Perspectives in Sustainable Agriculture and Environmental Technologies

Hayyawi W. A. Al-juthery 1*, Raad Farhan Shahad 1, Akram A. Hadi 2, Hassanein. H. Al-juthery 3

- ¹ College of Agriculture, University of Al-Qadisiyah, Iraq
- ² College of Al-Mussaib Technical, University of Al-Furat Al-Awsat Technical, Iraq
- ³ Al-Qasim Green University, Iraq

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ABSTRACT

Lately, there's been a growing global interest in nanoclays, which are essentially naturally layered silicate minerals. This attention is largely due to their unique chemical, physical, and even biological properties, not to mention their very large specific surface area. Because of their high aspect ratio and all that surface area, it's easier to modify their interfaces, which in turn helps improve things like soils and nutrient media. This review looks at some of the key clay minerals that are active in soil—think montmorillonite, hectorite, and kaolinite. We'll also go over some of the common ways their surfaces are modified to make them more compatible with different organic and mineral substances. From there, the discussion broadens to the wide range of industrial uses for these nanoclays, especially in agriculture. This includes everything from polymer nanocomposites and protective coatings to drug delivery, cleaning up environmental messes, creating flame-resistant materials, and even new packaging technologies. We'll also touch on recent progress in nanoclay research, with a particular focus on new developments in bio-nanomaterials and materials that respond to specific stimuli. Of course, there are still challenges to deal with, like getting the particles to disperse evenly, improving their surface interactions, and making sure they're environmentally safe. This work considers some potential strategies for tackling these issues to meet sustainability goals. Finally, this investigation wraps up by outlining where the field might be headed next. We're seeing emerging trends in nanoscience, like the design of multifunctional nanoclays and their integration into smart materials. These developments point to some really promising avenues for future scientific research and could lead to even more industrial applications in both agriculture and environmental management.

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INTRODUCTION

Nanoclays, a distinct category of layered silicate minerals that function at the nanoscale, have attracted growing interest within the materials * Corresponding Author Email: hayyawi.aljutheri@qu.edu.iq

science community over the past several years. This attention stems largely from their impressive structural, mechanical, and physicochemical properties. With their high aspect ratio, large

surface area, and ability to undergo intercalation, nanoclays have proven to be well-suited for improving the performance of a wide range of materials and systems [1]. Researchers have examined their potential applications in areas as varied as polymer nanocomposites, environmental cleanup, and biomedical engineering [2]. A substantial body of work has focused on strengthening the mechanical properties, thermal resistance, and barrier characteristics of polymer nanocomposites that incorporate nanoclays. When dispersed within polymer matrices, these materials exhibit markedly improved properties, making them attractive for use in the automotive, aerospace, and packaging industries [3]. The food packaging sector, especially, has seen notable gains from nanoclay-reinforced materials, which offer better protection against gas and penetration—ultimately extending the shelf life of perishable goods [4]. Nanoclays also show significant potential beyond purely structural uses, particularly in environmental and biomedical contexts. Their high cation exchange capacity and strong surface reactivity make them effective at adsorbing pollutants, which is useful in water treatment and soil remediation efforts [5]. Furthermore, because nanoclays are biocompatible and capable of interacting with biological molecules, they have drawn interest for applications in drug delivery, tissue engineering, and biosensor development [6]. The growing importance of nanoclays is mirrored in the expansion of the global nanoclay market, which is expected to reach roughly \$4.3 billion by 2030, driven by continued research progress and a widening array of industrial uses [7]. Such growth highlights the need for a thorough understanding of nanoclay properties, their applications, and future directions. This review focuses on the fundamental structural features of nanoclays, methods for their modification, and their multifunctional roles across different fields. It explains the mechanisms by which nanoclays enhance material properties and considers their place in emerging technologies. The article also addresses key issues facing current nanoclay research—such as achieving uniform dispersion and ensuring environmental safety—and suggests practical approaches for overcoming these obstacles. By bringing together recent findings, this review seeks to offer a forward-looking perspective on the future of nanoclays, with the aim of helping

researchers and industry practitioners fully realize their application potential.

NANOCLAYS: SCIENTIFIC CONCEPTS, APPLICATIONS, AND FUTURE PROSPECTS

Nanoclays are a class of nanostructured minerals—either naturally occurring synthetically modified—that belong mainly to the phyllosilicate family. Their layered morphology, high aspect ratio, significant cation exchange capacity, and large surface area have made them a subject of considerable scientific interest. From a structural standpoint, nanoclays consist of silicate layers typically organized in tetrahedraloctahedral-tetrahedral (T-O-T) configurations, with interlayer spaces that can be tailored using organic or inorganic agents to improve compatibility and overall functionality [8]. Properties such as thermal stability, mechanical reinforcement capability, and chemical resistance make nanoclays particularly attractive for use in polymer nanocomposites, environmental remediation, biomedical systems, sensors, and agricultural applications. As nanotechnology continues to advance and sustainable engineering becomes an increasingly important priority, nanoclays offer a cost-effective, abundant, and highly adaptable material platform for both current and future uses [1].

Structure and Types of Nanoclays

Nanoclays are generally derived from clay minerals such as montmorillonite (MMT), kaolinite, halloysite, and hectorite. These materials possess a characteristic layered structure, with individual layers roughly 1 nanometer thick and lateral dimensions ranging from tens of nanometers up to several micrometers [2]. Among the various types, montmorillonite stands out as particularly important and merits closer examination.

Montmorillonite (MMT)

Nano-montmorillonite refers to a nanostructured form of montmorillonite, a clay mineral in the smectite group that is defined by its 2:1 layered silicate architecture, often described as a tetrahedral-octahedral-tetrahedral (T-O-T) arrangement. In this configuration, a central alumina octahedral sheet is sandwiched between two silica-based tetrahedral sheets, resulting in plate-like layers separated by interlayer galleries—structural features that underpin its unique physicochemical behavior (Fig. 1).

Montmorillonite's high cation exchange capacity allows for the intercalation of surfactants or polymers, while also enabling the material to swell when exposed to water or polar solvents [3]. These attributes make montmorillonite an exceptionally versatile material, well suited to applications that demand enhanced interfacial interactions and structural tunability.

NANO-MONTMORILLONITE (NANO-MMT): **PROPERTIES AND APPLICATIONS**

Swelling and Intercalation Behavior

One of the most defining features of nano-MMT is its ability to swell when it comes into contact with water or polar solvents. This swelling occurs as solvent molecules and exchangeable cations penetrate the interlayer spaces, pushing the silicate layers apart and increasing the basal spacing. Within the interlayer region, hydrated exchangeable cations—commonly Na+, Ca2+, or Mg²⁺—are loosely bound and can be replaced relatively easily through cation exchange reactions. This mechanism offers a flexible platform for introducing surfactants, polymers, or bioactive compounds into the structure, which in turn modifies surface chemistry and broadens the functional capabilities of the nanoclay [4].

Structural Properties and Organic Modification Nano-MMT is characterized by a high specific surface area, a large aspect ratio, and notable cation exchange capacity (CEC), which generally falls in the range of 80 to 150 meq/100g. These properties facilitate the formation of intercalated or exfoliated nanocomposites when the material is blended with polymeric matrices, leading to marked improvements in mechanical, thermal, and barrier performance. Organic modification particularly through intercalation of quaternary ammonium salts-can convert nano-MMT into an organophilic form, allowing it to disperse in non-polar media and opening doors to advanced composite and biomedical uses [5].

Industrial Applications of Nano-MMT

Nano-MMT finds application across broad spectrum of industries. In polymer nanocomposites, it contributes to improved mechanical strength, flame resistance, and reduced permeability. For environmental remediation purposes, the material serves as an efficient adsorbent for heavy metals, organic contaminants, and dyes. In pharmaceutical delivery, nano-MMT enables controlled release of drugs and bioactive substances. The food packaging sector also benefits from its ability to enhance both mechanical properties and barrier performance in biopolymer films. Given its natural abundance, low cost, and multifunctionality, nano-MMT has become something of a cornerstone material

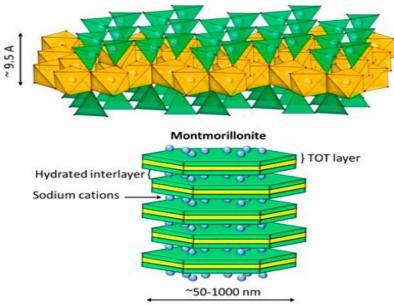


Fig. 1. Molecular containing exchangeable sodium structure of montmorillonite [8].

in both current and emerging nanotechnology applications [6].

HALLOYSITE NANOTUBES (HNTS)

Structure and Morphology

Nano-halloysite nanotubes (HNTs) are naturally occurring aluminosilicate nanoclays that belong to the kaolin mineral group. Unlike conventional layered clays such as montmorillonite, halloysite possesses a distinctive tubular shape that arises from the rolling of its 1:1 layered structure—consisting of one silica tetrahedral sheet bonded to one alumina octahedral sheet—into a hollow, multi-walled cylinder. These tubes typically measure around 50–70 nanometers in diameter and 1–2 micrometers in length [7]. The tubular geometry gives HNTs a set of properties quite different from those of traditional layered silicate clays, making them especially useful in applications where controlled nanostructures are required.

Applications and Significance

The unique morphology and surface characteristics of halloysite nanotubes make them well suited for drug delivery and nanoencapsulation. The hollow core of the tubes

provides a natural compartment for loading pharmaceutical compounds and releasing them in a controlled manner, while the outer surface can be chemically modified to improve biocompatibility and enable targeted delivery [8]. HNTs also show promise in areas beyond biomedicine, including reinforced composites, environmental cleanup, and cosmetic formulations—applications that continue to expand their relevance in modern nanotechnology.

Structural Dimensions and Physicochemical Properties of Halloysite Nanotubes

In terms of dimensions, halloysite nanotubes generally have outer diameters between 50 and 70 nanometers, inner lumen diameters of about 10 to 20 nanometers, and lengths ranging from 1 to 2 micrometers, although these values can vary depending on the source material and how the sample is purified. This nanotubular structure affords HNTs several advantages, including a high aspect ratio, dual-surface chemistry with silicarich exterior and alumina-rich interior surfaces, and considerable mechanical strength [9]. These structural characteristics set HNTs apart from conventional layered silicate clays and position

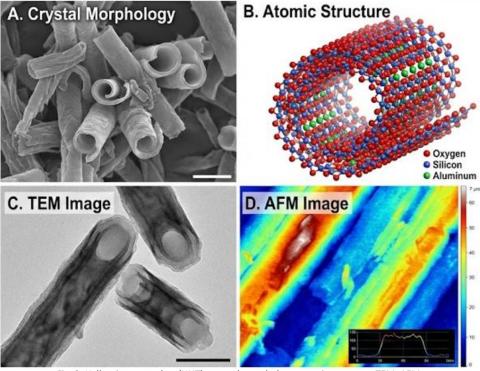


Fig. 2. Halloysite nanotubes (HNT) - crystal morphology, atomic structure, TEM, AFM.

them as specialized nanomaterials with unique functional potential.

NANOENCAPSULATION AND CONTROLLED RELEASE PROPERTIES

The hollow lumen of HNTs essentially functions as a nanocontainer, capable of holding a variety of functional molecules. This makes them suitable for nanoencapsulation, controlled release, and protecting sensitive compounds from environmental degradation. Such capabilities have generated significant interest in using HNTs for pharmaceutical delivery, particularly for sustained or targeted release of drugs, antimicrobial agents, and other bioactive substances [10]. Notably, the inner and outer surfaces of the tubes can be modified independently through chemical functionalization, which greatly enhances the material's versatility. This dual-surface modification capability is a distinguishing feature of HNTs and expands their potential for use in sophisticated biomedical and industrial contexts (Fig. 2).

Diverse Applications Beyond Biomedical Fields

Halloysite nanotubes have proven useful in a number of sectors outside of biomedicine. In

nanocomposite materials, HNTs act as reinforcing fillers within polymer and biopolymer matrices, substantially boosting mechanical strength and thermal stability. They also function as effective adsorbents in environmental remediation, capturing heavy metals, organic pollutants, and petroleum-based contaminants. In advanced coatings and packaging, HNTs facilitate controlled release of corrosion inhibitors and antimicrobial agents, helping to extend both material durability and product shelf life [11].

Environmental Sustainability and Future Potential

Halloysite nanotubes are naturally abundant, exhibit low toxicity, and are both biocompatible and biodegradable—qualities that make them eco-friendly and cost-effective nanomaterials with strong potential for industrial and biomedical applications (Fig. 3). These characteristics align well with current sustainability goals, which is part of why HNTs have attracted attention as candidates for developing environmentally responsible nanotechnological solutions. Given their inherent properties and functional adaptability, it seems likely that HNTs will take on an increasingly important role in advancing both existing and next-generation applications across a wide range

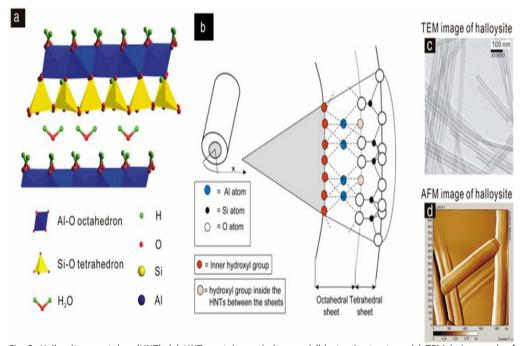


Fig. 3. Halloysite nanotubes (HNT). (a) HNT crystal morphology and (b) atomic structure, (c) TEM (micrograph of transmission electron microscopy), and (d) AFM (atomic force microscopy).

of scientific and industrial fields [12].

KAOLINITE: STRUCTURE, PROPERTIES, AND APPLICATIONS

Structural Characteristics and Limitations

Nano-kaolinite is a naturally occurring 1:1 phyllosilicate nanoclay made up of alternating silica tetrahedral and alumina octahedral sheets. Unlike smectite clays like montmorillonite, kaolinite does not swell—a consequence of the strong hydrogen bonding between its adjacent layers, which locks the interlayer spacing in place and greatly limits its intercalation potential [13]. This structural limitation sets kaolinite apart from more reactive clay minerals and largely determines how it performs in different applications.

Mechanical Reinforcement Potential

Even though nano-kaolinite has limited intercalation capacity, it offers a number of notable advantages—particularly its high crystallinity, strong chemical inertness, and mechanical stability—which make it a useful additive for mechanical reinforcement in a variety of composite materials. At the nanoscale, kaolinite particles exhibit increased aspect ratios, better dispersion behavior, and greater surface area, all of which contribute to effective stress transfer and

improved interfacial adhesion when blended into polymeric matrices [14]. The plate-like shape of kaolinite, with thicknesses on the nanometer scale and lateral dimensions ranging from hundreds of nanometers to several micrometers, plays a significant role in its reinforcing capability.

Surface Modification and Compatibility Enhancement

While the intrinsic resistance to interlayer swelling limits kaolinite's capacity to intercalate large organic molecules, surface modifications—such as acid treatment or grafting with functional groups—can substantially improve its compatibility with both organic and aqueous systems [15]. These chemical treatments enhance the surface reactivity and interfacial interactions, thereby expanding the material's utility in advanced applications requiring specific chemical or physical properties.

Industrial and Environmental Applications

Nano-kaolinite demonstrates considerable utility across multiple industrial sectors. In polymer nanocomposites, it functions as a reinforcing agent, improving tensile strength, elastic modulus, and thermal resistance. Within ceramics and paint formulations, nano-kaolinite enhances

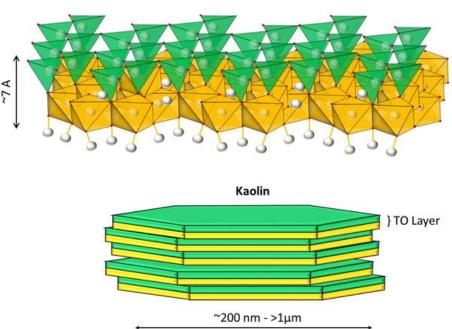


Fig. 4. Kaolinite structure. The green sheet indicates the tetrahedral silica layer (T), and the yellow sheet represents the octahedral alumina layer (O).

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durability, dimensional stability, and surface smoothness (Fig. 4). For bio-based packaging materials, it contributes to structural integrity and improves gas barrier properties. In catalytic and adsorption applications, nano-kaolinite serves as a support matrix for catalysts or as a sorbent following surface functionalization [16]. The abundance, cost-effectiveness, non-toxicity, and environmental stability of nano-kaolinite position it as an attractive alternative to synthetic nanofillers in green materials and environmentally responsible engineering applications.

LAPONITE: SYNTHETIC HECTORITE AND ITS APPLICATIONS

Introduction and Overview

Nano-Laponite is a synthetic form of hectorite, a layered silicate mineral known for its uniform particle size and high purity (Fig. 5). It has drawn considerable attention across various industries, especially those that require precise control over viscosity and flow behavior [17]. The unique properties of nano-Laponite make it a highly versatile nanomaterial for rheological modification and biomedical uses.

Structural Properties and Colloidal Behavior
Nano-Laponite has a platelet-like structure

that contributes significantly to its gel-forming ability and its capacity to modulate rheological properties. Particles typically range from 25 to 50 nanometers in diameter and take the form of disc-shaped nanocrystals arranged in a silica tetrahedral—alumina octahedral—silica tetrahedral configuration [18]. This structural arrangement allows nano-Laponite to interact effectively with solvents, producing stable colloidal systems that are useful in a variety of applications. The layered architecture can also be modified through intercalation, exfoliation, or surface functionalization, improving dispersion in hydrophobic matrices and enabling new functionalities [19].

Rheological Control and Industrial Applications

Nano-Laponite is widely used for thickening, suspension stabilization, and viscosity modification—particularly in paints, coatings, personal care products, and industrial processes where controlled fluid behavior is essential [20]. Its effectiveness in altering the rheological properties of liquids makes it especially valuable in formulations requiring precise fluid consistency. The fact that desired viscosity profiles can be achieved with relatively small amounts of additive also makes nano-Laponite economically appealing

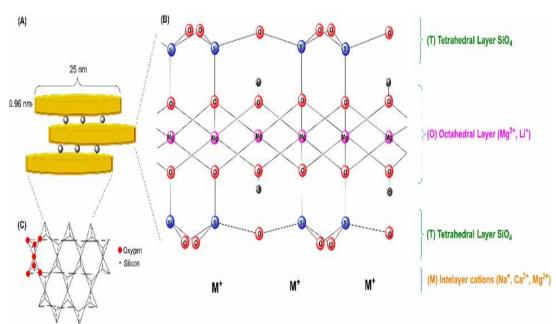


Fig. 5. Layer structure of an hectorite-like clay with nanocrystals with a disc-like morphology and the arrangement of Si-O tetrahedral layers Hectorite clay forms nanoscaled platelets with a diameter ranging from 25-50 nm. It has a layer structure that allows it to interact with a solvent.

for large-scale industrial use.

Biomedical Applications and Drug Delivery

biocompatibility of nano-Laponite has sparked considerable research interest in biomedical formulations. It has been explored extensively for drug delivery systems, tissue engineering scaffolds, and other biomedical applications [21]. Because nano-Laponite can encapsulate and release pharmaceutical compounds in a controlled, sustained manner, it has emerged as a promising candidate for controlled-release drug delivery and targeted therapies. Its compatibility with biological systems, along with tunable release kinetics, offers significant advantages for advanced pharmaceutical formulations.

Purity, Stability, and Quality Assurance

The high purity of nano-Laponite contributes to its stability and reduces the risk of introducing impurities or unwanted side effects in sensitive formulations such as pharmaceuticals and cosmetics [22]. Consistent physicochemical properties are critical for maintaining the quality and reproducibility of final products. As a synthetically manufactured material, nano-Laponite can be produced under strict quality control with high batch-to-batch consistency, ensuring reliability across a wide range of applications.

Sustainability and Biocompatibility

The non-toxic and biocompatible nature of nano-Laponite makes it well suited for environmentally conscious and safety-critical applications [23]. Its synthetic origin allows for controlled manufacturing processes that eliminate the variability associated with natural mineral sources, resulting in reproducible performance and improved safety profiles. These characteristics position nano-Laponite as an attractive alternative to conventional additives in green chemistry and sustainable engineering efforts.

APPLICATIONS OF NANOCLAYS

Polymer Nanocomposites

Nanoclays are commonly used as fillers in polymeric matrices to improve thermal stability, mechanical strength, and barrier properties. When properly dispersed, they create a tortuous diffusion pathway for gases and moisture, which

significantly enhances the performance of packaging materials [24]. Incorporating nanoclays into biopolymer systems has shown considerable promise, yielding improved food packaging films with antimicrobial activity and longer shelf life [25]. These improvements make nanoclay-reinforced polymers particularly useful for applications that demand stringent barrier performance and extended product durability.

Biomedical Applications

In recent years, nanoclays have attracted growing interest in biomedical sciences due to their biocompatibility, low toxicity, and favorable surface chemistry. Their versatility in biomedical contexts spans several domains. Halloysite and montmorillonite nanotubes, for instance, serve as effective carriers for controlled pharmaceutical release by encapsulating molecules within their tubular or interlayer compartments [26]. In tissue engineering, nanoclay-reinforced scaffolds improve mechanical integrity while promoting cellular adhesion and proliferation [27]. Nanoclay composites have also been incorporated into electrochemical sensor platforms, where they enhance signal stability and improve specificity for analyte detection [28]. Taken together, these properties make nanoclays exceptionally versatile materials for advanced biomedical innovations.

Environmental Remediation

The strong adsorption capacity of nanoclays makes them highly effective for removing heavy metals, organic dyes, and pharmaceutical residues from contaminated water. Modified nanoclay formulations have been specifically designed to improve selectivity for targeted pollutants and allow for regeneration of the adsorbent. modified Montmorillonite with surfactant molecules, for example, has shown excellent efficiency in removing dyes from textile wastewater, addressing a significant environmental issue in the textile industry [29]. These applications highlight the potential of nanoclays for developing cost-effective and sustainable water treatment solutions.

Agriculture and Soil Management

One notable innovation in agricultural nanotechnology is the development of liquid nanoclay formulations, which allow fine nanoclay particles to interact effectively with



soil mineral constituents. This technology significantly improves water retention and nutrient-holding capacity in arid and semi-arid soils [30] (Fig. 6). Liquid nanoclay formulations have been successfully applied in desert farming contexts, demonstrating their practical value for boosting agricultural productivity in water-limited regions. Integrating nanoclay technology into soil management practices represents a promising approach for sustainable agriculture and environmental restoration under challenging climatic conditions.

STRUCTURE AND CRYSTALLINE TYPES OF NANOCLAYS

Nanoclays are nanometer-scale layered silicate minerals with thicknesses around 1 nanometer and lateral dimensions ranging from tens to several hundred nanometers. They consist of stacked silicate sheets arranged in layered configurations, with interlayer spaces that can accommodate various ions or molecules. The fundamental structural organization of nanoclays reflects two main crystalline arrangements: 1:1 layer structures made up of one tetrahedral sheet and one octahedral sheet (as seen in kaolinite), and 2:1 layer structures consisting of two tetrahedral sheets surrounding a central octahedral sheet (as in montmorillonite and hectorite) [31]. The layered

architecture is held together by weak van der Waals interactions, which facilitate ion exchange and intercalation with organic molecules, allowing for modification and customization of nanoclay properties for specialized applications [32].

Montmorillonite (MMT)

Montmorillonite is the most widely studied and industrially utilized nanoclay. A member of the smectite mineral group, MMT features a 2:1 layered structure with high surface area and significant cation exchange capacity. Its ability to swell in water and intercalate organic cations or polymer chains between its layers enables enhanced dispersion within composite matrices [33]. MMT is used extensively in polymer reinforcement, packaging materials, and wastewater treatment, reflecting its versatility and effectiveness across multiple industrial sectors [34].

Halloysite Nanotubes (HNTs)

Halloysite is a naturally occurring aluminosilicate mineral with a 1:1 layered structure that sets it apart from planar nanoclay minerals. Unlike conventional layered nanoclays, halloysite typically forms hollow nanotubes with diameters of 50 to 70 nanometers and lengths between 1 and 2 micrometers. This distinctive tubular morphology makes HNTs particularly

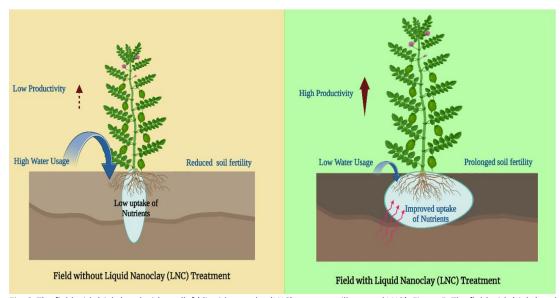


Fig. 6. The field with (right) and without (left) liquid nanoclay (LNC) treatment illustrated LNC's Figure 5. The field with (right) and without (left) liquid nanoclay (LNC) treatment illustrated LNC's impact on soil, nutrient, water management, and environmental sustainability.

well suited for pharmaceutical delivery systems, nano-encapsulation, and controlled-release formulations [35]. The internal and external surfaces of HNTs can be independently modified through chemical functionalization, enabling multifunctional applications and improved performance [36].

Kaolinite

Kaolinite is a non-swelling 1:1 layered aluminosilicate mineral with limited intercalation capability but high chemical stability and mechanical strength. In contrast to montmorillonite, kaolinite lacks the pronounced ion exchange properties characteristic of more

reactive clay minerals. It has traditionally been used as a reinforcing filler in ceramics, paper manufacturing, and paints, and more recently has shown promise in biocompatible systems when appropriately modified [37]. Its mechanical robustness and chemical inertness make it valuable for applications requiring durability and resistance to chemical degradation.

Hectorite

Hectorite is a trioctahedral smectite clay mineral structurally similar to montmorillonite but with magnesium as the central octahedral ion. This compositional difference gives hectorite unique properties that make it especially useful

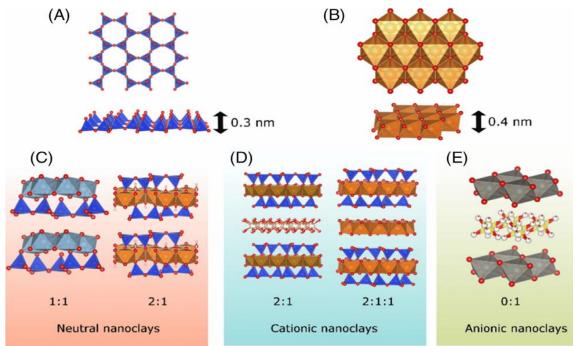


Fig. 7. (a) Tetrahedral sheet; (b) octahedral sheet. Layered nanoclay structures: (c) neutral nanoclays (type 0:1 and 2:1), (d) cationic nanoclays (type 0:1).

Table 1. Comparative Properties of Major Nanoclay Types.

Nanoclay Type	Layer Structure	Particle Dimensions	CEC (meq/100g)	Key Properties	Primary Applications Polymer nanocomposites, water treatment, drug delivery	
Montmorillonite (MMT)	2:1 (T-O-T)	~1 nm thick, 100- 500 nm lateral	80-150	High swelling, intercalation capacity		
Halloysite (HNTs)	1:1 rolled	50-70 nm OD, 1-2 μm length	10-40	Tubular morphology, dual surface chemistry	Nanoencapsulation, controlled release, reinforcement	
Kaolinite	1:1	~0.7 nm thick, 0.1- 4 µm lateral	3-15	Non-swelling, high crystallinity	Ceramics, paper, mechanical reinforcement	
Laponite (Hectorite)	2:1 (T-O-T)	25-50 nm diameter, 1 nm thick	50-55	Synthetic, high purity, gel-forming	Rheology control, cosmetics, biomedical	

in cosmetic formulations, pharmaceutical applications, and nanocomposite systems owing to its excellent dispersibility in both aqueous and organic solvents [38]. Synthetic variants like Laponite are widely used for rheological control and in hydrogel formulations, underscoring the commercial importance of this class of clay minerals [39] (Table 1).

Synthetically Modified Nanoclays

To improve dispersion in non-polar media and enhance interfacial bonding with polymeric matrices, nanoclays are often subjected to organic modification. This is typically done by intercalating surfactant molecules—particularly quaternary ammonium salts—into the interlayer galleries of montmorillonite, converting them into organoclays with increased hydrophobic character [40]. These chemically modified nanoclays show substantially improved compatibility with hydrophobic polymers and are widely used in developing high-performance nanocomposites with enhanced mechanical and thermal properties [41] (Fig. 7).

MANUFACTURING METHODS FOR NANOCLAYS

Nanoclays, including synthetic variants like nano-Laponite and other nanostructured clay formulations, are produced using a range of methods, each of which influences the properties and functional characteristics of the final product. Manufacturing approaches generally aim to reduce clay particle size to the nanoscale while ensuring uniformity and high purity. The main manufacturing techniques fall into two broad categories: top-down methods and bottom-up methods [42].

Top-Down Methods

Top-down manufacturing involves breaking down larger clay particles into nanosized components. Common top-down techniques include mechanical milling and solvent-based exfoliation. Mechanical milling uses high-energy ball mills or similar equipment to grind bulk clay into fine particles [43]. While this method can produce nanoclays, it often results in non-uniform particle size distributions. Exfoliation in solvents, on the other hand, involves separating clay platelets into individual sheets, typically by dispersing clay in a solvent under high shear or sonication [44]. This yields a dispersion of nanoclays in a liquid

medium, which facilitates further processing and application.

Bottom-Up Methods

Bottom-up manufacturing involves synthesizing nanoclays from molecular precursors. The sol-gel process is one important bottom-up approach, in which precursor solutions undergo hydrolysis and condensation reactions to form clay nanoparticles [45]. This method allows for production of nanoclays with controlled particle dimensions and high purity. Chemical vapor deposition (CVD) is another bottom-up technique, where precursor gases are deposited onto a substrate to form thin films or nanoparticles of clay minerals [46]. CVD enables precise control over particle size and morphology.

Intercalation and Exfoliation Methods

Intercalation-based manufacturing involves introducing molecules—such guest surfactants—into the interlayer spaces of clay minerals, followed by exfoliation to produce nanosheets [47]. This approach can significantly increase surface area and dispersibility. Surfactantmediated intercalation, in which organic cations or surfactant molecules are inserted into interlayer spaces, leads to exfoliation into nanosheets and is commonly used in the production of nano-Laponite and similar nanoclays [48]. Hydrothermal synthesis is another manufacturing method, involving heating precursor solutions under elevated pressure and temperature in sealed vessels (autoclaves) [49]. The high-temperature conditions promote crystallization of clay nanoparticles from solution.

NANOCLAYS IN NANOFERTILIZER FORMULATIONS Introduction to Nanofertilizers

Nanofertilizers, which use nanotechnology to improve nutrient delivery to crops, are gaining increasing attention for their potential to transform modern agricultural practices [50]. These advanced formulations offer improved nutrient use efficiency, reduced environmental losses, and enhanced crop productivity compared to conventional fertilizers [51]. Among the various nanomaterials used in nanofertilizer development, nanoclays—particularly montmorillonite and halloysite nanotubes—have emerged as especially promising nutrient carriers due to their high surface area, significant cation exchange capacity,

and ability to intercalate nutrient ions [52].

Structural Properties and Advantages

Nanoclays function as nano-sized layered mineral silicates, composed primarily of montmorillonite, kaolinite, and halloysite minerals. They exhibit characteristic layered structures with interlayer spaces that can accommodate various guest molecules or ions [53]. Key properties that make nanoclays suitable for nanofertilizer applications include high surface area, which enhances nutrient adsorption and interaction with plant roots; significant cation exchange capacity, allowing for binding and gradual release of nutrient ions; and biocompatibility combined with low toxicity, ensuring environmental safety [54].

Controlled Nutrient Release Mechanisms

Nanoclays allow for encapsulation or adsorption of nutrient molecules within their layers or on their surfaces, forming nanocomposites that release nutrients in a controlled, sustained manner [61]. This mechanism maintains nutrient availability over longer periods, reducing the need for frequent fertilizer applications. Montmorillonite and halloysite nanotubes are particularly effective at encapsulating both macronutrients and micronutrients—studies have shown that nitrogen, potassium, and micronutrients like zinc and iron can be loaded into nanoclay matrices and released gradually in soil environments [56]. Research indicates that urea loaded onto montmorillonite releases nitrogen more slowly and steadily than conventional urea formulations, resulting in improved nitrogen uptake and better plant growth [57].

Environmental and Agronomic Benefits

Nanoclay carriers significantly reduce nutrient leaching into water systems by binding nutrients electrostatically and physically within interlayer spaces, preventing rapid release and minimizing environmental contamination [58]. Additionally, nanoclays can have positive effects on soil structure and promote beneficial microbial activity, and unlike synthetic polymer-based fertilizers, they do not introduce persistent residues into soil ecosystems, making them more sustainable [59]. Despite their considerable potential, the use of nanoclays in agriculture remains limited by challenges such as cost-effective production, regulatory considerations, and scalability [60].

Nevertheless, ongoing advances in materials science and nanotechnology are expected to address these limitations.

NANOCLAYS IN NANO-BIOFERTILIZER DEVELOPMENT

Overview and Significance

Agriculture is undergoing transformative advancement through nanotechnology integration, which promises enhanced productivity while reducing environmental impacts. Nanobiofertilizers—biofertilizers enhanced through incorporation—represent nanomaterial significant innovation in this domain. Nanoclays, constituting a group of naturally occurring or synthetically modified aluminosilicate minerals, have garnered considerable attention for their capacity to improve biofertilizer formulations owing to their elevated surface area, pronounced ion exchange capacity, biocompatibility, and environmental benignity [61]. These layered silicates, typically composed of montmorillonite, kaolinite, halloysite, and bentonite, exhibit nanoscale dimensions in at least one direction and possess elevated aspect ratios and swelling capacities [62].

Nanoclays as Microbial Carrier Matrices

A primary application of nanoclays in nanobiofertilizer production involves their utilization as carriers for beneficial microorganisms, including nitrogen-fixing bacteria (such as Rhizobium and Azotobacter) and phosphate-solubilizing bacteria (PSB) [63]. Nanoclays provide a protective matrix that maintains microbial viability and facilitates gradual colonization of plant roots. Montmorillonite-based nanoformulations have demonstrated effectiveness in delivering Azospirillum and Bacillus strains, exhibiting enhanced root colonization and nitrogen uptake in crop systems [64]. The elevated water retention capacity and pronounced cation exchange capacity of nanoclays establish a conducive microenvironment for microbial survival.

Sustained Release and Environmental Protection

Nanoclays enable controlled and sustained release of nutrients and microbial metabolites through their interlayer spacing and surface functional groups, which respond to environmental triggers such as pH, temperature, or moisture variations [65]. This property proves crucial in



reducing nutrient leaching and volatilization, thereby increasing nutrient use efficiency. Research demonstrates that nano-biofertilizers incorporating halloysite nanotubes exhibited a 40% increase in phosphorus uptake by plants due to the slow and sustained release of phosphate-[67]. solubilizing microbes Furthermore, nanoclays provide protection to sensitive bioactive compounds and microorganisms from environmental degradation including UV radiation, and temperature fluctuations, desiccation, thereby improving shelf-life and field efficacy of biofertilizer formulations [68]. Studies indicate that nano-biofertilizers formulated with kaolinite retained microbial viability for extended periods exceeding six months without refrigeration, with significant implications for distribution and storage in resource-limited settings [69].

Enhancement of Plant Growth and Soil Health

Nanoclays improve soil structure, water-holding capacity, and microbial activity, all of which positively influence plant development. Their interaction with the rhizosphere fosters improved nutrient cycling and microbial colonization [70]. Nano-biofertilizers incorporating nanoclay matrices have demonstrated enhanced uptake of macro and micronutrients by plants, resulting in improved biomass accumulation and yield enhancement [71]. Crops treated with nanoclay-based formulations of plant growth-promoting rhizobacteria (PGPR) exhibited a 25% increase in

growth relative to conventional treatments [72].

Functionalization for Targeted Applications

Nanoclays can be functionalized with biopolymers or surfactant compounds to address specific nutrient deficiencies or crop requirements, enabling the development of "smart fertilizers" that release their contents in response to crop signals or environmental conditions [73]. Layered double hydroxides (LDHs) functionalized with amino acids have been employed to deliver both nitrogen and micronutrients, improving chlorophyll content and photosynthetic efficiency in wheat crops [74].

Sustainability and Economic Advantages

Nanoclays are abundant, cost-effective, and environmentally benign, rendering them suitable for sustainable agricultural practices. Their utilization reduces dependence on chemical fertilizers, minimizes environmental pollution, and supports organic farming methodologies [75]. Moreover, owing to their controlled-release properties, the overall quantity of fertilizer required is substantially reduced, thereby lowering production and application costs [76].

METHODS OF APPLYING NANOCLAYS IN AGRICULTURAL SYSTEMS

The increasing need for sustainable agricultural practices has spurred interest in nanotechnology

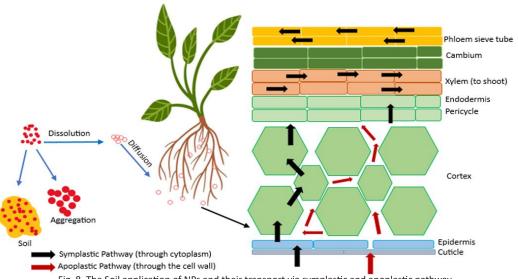


Fig. 8. The Soil application of NPs and their transport via symplastic and apoplastic pathway.

within farming systems. Among the various nanomaterials being explored, nanoclays—especially montmorillonite, halloysite, kaolinite, and bentonite—show particular promise due to their environmental compatibility and cost-effectiveness [77]. Nanoclays are characterized by layered silicate structures with nanometric thickness and micrometric lateral dimensions, which make them well suited as carriers and protective agents in agricultural settings. How nanoclays are applied is critical to optimizing their performance and ensuring they are used safely and effectively. This section reviews major delivery strategies and outlines both current and potential agricultural applications.

Soil Amendment

One of the most common methods for applying nanoclays is direct incorporation into soil. This can be done through broadcasting or localized placement during tillage or planting, which helps improve soil structure, water-holding capacity, and cation exchange capacity [78]. Research has shown that montmorillonite added to sandy soil led to a 20–30% increase in moisture retention along with improved root development in crop systems [79] (Fig. 8).

Foliar Application

Nanoclays can also be suspended in water and

sprayed directly onto plant foliage, often as part of nutrient formulations or protective coatings. This method delivers nutrients or protective agents directly to plant tissues [80] (Fig. 9). For example, halloysite nanotube-based formulations applied to wheat foliage to supply zinc resulted in significant improvements in chlorophyll content [81].

Seed Coating and Priming

Seeds can be treated with nanoclay suspensions before sowing to promote germination and early growth. This approach allows micronutrients or beneficial microorganisms to be delivered during early developmental stages [82]. Seed coating with nanoclay and Azospirillum increased germination rates by 18% and enhanced seedling vigor in maize [83].

Encapsulation of Biofertilizers

Nanoclays can encapsulate microbial inoculants or bioactive compounds to create nano-biofertilizers. This protects microorganisms, ensures sustained nutrient release, and improves colonization within the rhizosphere [84]. Montmorillonite-encapsulated phosphate-solubilizing bacteria, for instance, improved phosphorus uptake in rice cultivation [85].

NANOCLAY-POLYMER COMPOSITES

Nanoclays can be incorporated into biopolymer

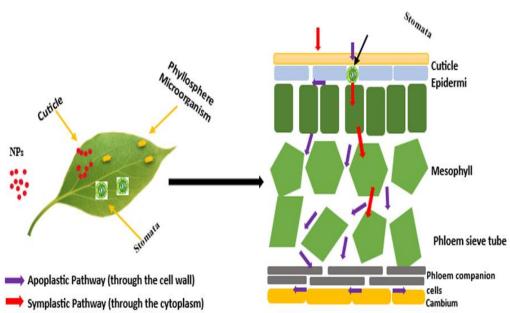


Fig. 9. Foliar applications of NPs and transport via apoplastic and symplastic pathway.

matrices such as chitosan or starch for controlled nutrient release. These composites act as intelligent delivery systems that respond to environmental triggers like pH or moisture changes [86]. Chitosannanoclay composites released nitrogen over a 30-day period and reduced leaching losses by 40% [87].

Irrigation Integration

Nanoclays can be introduced into irrigation systems as colloidal suspensions, allowing for uniform delivery through water. This approach enables precision delivery of nutrients or microbial products [88]. Bentonite nanoclay suspension applied through drip irrigation systems improved nutrient use efficiency and crop yield in tomato cultivation [89].

AGRICULTURAL APPLICATIONS OF NANOCLAYS

Soil Conditioning and Remediation

Nanoclays improve physical soil properties such as porosity and water-holding capacity. They also help immobilize heavy metals, reducing their bioavailability [90]. Kaolinite-amended soils, for example, reduced cadmium uptake in spinach by 35% [91].

Controlled Release of Fertilizers

The interlayer spaces of nanoclays allow for encapsulation of nutrients with gradual, sustained release over time [92]. Urea intercalated within montmorillonite matrices released nitrogen over 21 days, improving nitrogen use efficiency by 45% in wheat [93].

Pest and Disease Management

Nanoclays serve as carriers for pesticides, herbicides, and fungicides, reducing application rates and frequency [94]. Halloysite nanotubes

loaded with neem oil provided sustained release of biopesticides and substantially reduced aphid infestation in okra [95].

Enhancement of Plant Growth and Yield

By improving nutrient delivery and stress resistance, nanoclays contribute to higher crop productivity [96]. Foliar application of nanoclay-based zinc fertilizers increased maize yield by 22% compared to conventional zinc sulfate formulations [97].

Microbial Carriers for Bioinoculants

Nanoclays protect beneficial microorganisms from UV radiation, desiccation, and pH extremes, thereby improving their viability and activity [98]. Encapsulation of Rhizobium within nanoclay matrices resulted in a twofold increase in nodulation in soybean [99].

Environmental and Safety Considerations

Nanoclays are generally considered environmentally benign because of their natural origin and low toxicity. However, their interactions with soil biota, particularly at high concentrations, need further study [100]. Some research suggests that excessive nanoclay application could disrupt microbial communities, highlighting the need for controlled application protocols and environmental monitoring [101] (Table 2).

Physiological Effects of Nanoclays on Plant Tissues

Advances in agricultural nanotechnology have introduced a variety of nanomaterials aimed at promoting plant health and productivity. Nanoclays—naturally occurring aluminosilicate minerals reduced to nanoscale dimensions—are widely used because of their biocompatibility, structural versatility, and potential as nutrient

Table 2. S	Summary of Nanocl	ay Applications in	Agriculture with	Quantitative Outcome	es.
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Application	Nanoclay Type	Crop/System	Key Outcome	Improvement (%)	Reference
Soil amendment	Montmorillonite	Sandy soil	Moisture retention	20-30% increase	[84]
Foliar Zn delivery	Halloysite NTs	Wheat	Chlorophyll content	Significant increase	[86]
Seed coating	Nanoclay + Azospirillum	Maize	Germination rate	18% increase	[88]
P-solubilizing bacteria carrier	Montmorillonite	Rice	Phosphorus uptake	Enhanced	[90]
Controlled N release	Chitosan-nanoclay	General	Leaching reduction	40% decrease	[92]
Drip irrigation	Bentonite nanoclay	Tomato	NUE and yield	Improved	[94]
Heavy metal immobilization	Kaolinite	Spinach	Cd uptake reduction	35% decrease	[96]
Slow-release urea	Montmorillonite	Wheat	N use efficiency	45% increase	[98]
Biopesticide delivery	Halloysite NTs + neem oil	Okra	Aphid infestation	Substantial reduction	[100]
Zn foliar application	Nanoclay-based	Maize	Grain yield	22% increase	[102]
Rhizobium encapsulation	Nanoclay matrix	Soybean	Nodulation	2-fold increase	[104]

carriers [102]. Understanding how nanoclays affect plant physiological processes at the tissue and cellular level is important, as these effects can range from enhanced nutrient absorption to changes in stress physiology and, in some cases, cytotoxic effects under certain conditions [103].

UPTAKE AND TRANSLOCATION MECHANISMS

Nanoclays interact with plant tissues either through direct contact (such as foliar sprays) or indirectly via soil or seed treatments. Due to their small size and charge characteristics, nanoclay particles can penetrate root epidermal cells or adhere to leaf cuticles, where they may be absorbed and translocated through vascular tissues [104]. Montmorillonite nanoparticles applied to wheat were detected in both root and shoot tissues, indicating systemic movement [105]. This translocation capacity raises important questions about their physiological influence beyond the site of application.

Effects On Germination and Early Development

Several studies have documented stimulatory effects of nanoclays on seed germination and early seedling development. Montmorillonite and halloysite nanotube treatments significantly

increased water uptake in seeds, accelerating germination and radicle emergence in crops like maize and rice [106]. Enhanced root elongation and shoot biomass were observed in barley seeds primed with nanoclay suspensions, likely due to improved nutrient availability and water retention [107]. However, at elevated nanoclay concentrations (above 200 mg/L), germination was sometimes inhibited, possibly because of altered water potential or mechanical interference with seed coat permeability [108].

Impact on Nutrient Uptake and Photosynthetic Performance

Nanoclays improve nutrient availability and absorption, which in turn enhances photosynthetic performance [109]. Halloysite nanotubes loaded with micronutrients such as zinc and iron improved chlorophyll synthesis and photosystem efficiency in tomato and wheat plants [110]. Plants treated with kaolinite-based nanoformulations showed increased leaf chlorophyll content and net photosynthetic rate owing to improved nutrient balance and stomatal regulation [111]. These physiological improvements are often linked to nanoclays' cation exchange capacity and their ability to retain nutrients near root zones,

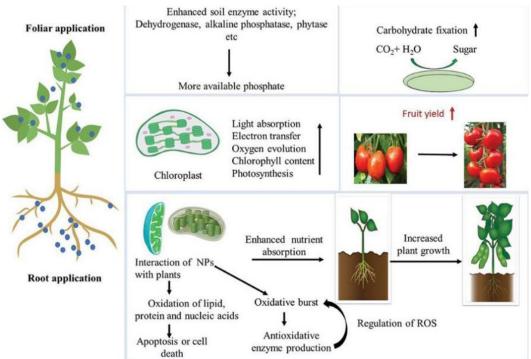


Fig. 10. Effect of foliar and root application of NPs on the growth and yield of plants.

facilitating consistent nutrient uptake.

Influence on Enzymatic and Antioxidant Activities

Nanoclays can modulate enzymatic activity and the antioxidant defense system in plant tissues [112]. Nanoclay-treated soybean plants exhibited elevated activity of catalase (CAT), peroxidase (POD), and superoxide dismutase (SOD), indicating enhanced antioxidative responses [113]. These changes suggest that nanoclays may induce mild oxidative stress, priming plant defense mechanisms—a phenomenon known as hormesis [114] (Fig. 10). At optimal concentrations, these effects are beneficial, enhancing plant resilience to abiotic stresses such as drought or salinity. However, excessive nanoclay exposure may overwhelm antioxidant systems and cause cellular damage.

Cellular and Anatomical Effects

Histological studies have revealed both beneficial and adverse modifications at the cellular level. Montmorillonite application increased vascular bundle diameter and xylem thickness in treated rice stems, suggesting improved nutrient transport [115]. Transmission electron microscopy (TEM) showed nanoclay particles within leaf mesophyll cells, occasionally associated with minor organellar disruption at elevated concentrations [116]. In some cases, exposure to high nanoclay doses induced plasmolysis, vacuole swelling, and mitochondrial deformities, indicating potential cytotoxicity [117].

Stress Tolerance Enhancement

Nanoclays enhance tolerance to abiotic stress by stabilizing cell membranes, regulating water balance, and improving antioxidative capacity [118]. Kaolinite-treated plants exhibited higher relative water content and reduced electrolyte leakage under drought stress [119]. Under salinity stress, halloysite-nanoclay formulations helped maintain K*/Na* homeostasis, which is critical for salt stress adaptation [120].

Toxicological Considerations

While nanoclays are generally considered safe and biodegradable, there is growing awareness of dose-dependent toxicity [121]. High levels may disrupt cell division, induce DNA damage, or interfere with metabolic enzyme function [122]. Long-term accumulation in plant tissues and

ecotoxicological impacts on soil microbes and higher trophic levels remain insufficiently studied. As a result, eco-toxicological screening and establishment of threshold limits for agricultural use are essential [123].

ROLE OF NANOCLAYS IN PLANT GROWTH AND YIELD ENHANCEMENT

Nanoclays, particularly montmorillonite-based nanomaterials, have attracted considerable attention in agriculture due to their distinctive physicochemical properties, including high surface area, significant cation exchange capacity, and swelling behavior [124]. These properties contribute to improved nutrient retention, waterholding capacity, and controlled fertilizer release, all of which can enhance plant growth and yield.

Enhanced Nutrient Retention and Release

Nanoclays function as fertilizer carriers, enabling slow and targeted nutrient release. This reduces nutrient leaching while improving nutrient availability to plants [125]. Incorporating nano-clay in fertilizer formulations substantially improved nitrogen use efficiency in wheat, resulting in increased biomass and grain yield [126].

Improved Soil Water Retention

Nanoclays enhance soil texture and increase water-holding capacity, which is particularly beneficial under drought conditions [127]. Nanoclay application in arid soils improved soil moisture content and supported better crop performance in maize and barley [128].

Stimulation of Plant Growth and Development

Nanoclays may stimulate physiological responses in plants by modulating hormonal balance and root development [129]. Foliar application of nano-clay enhanced chlorophyll content, photosynthetic rate, and overall plant vigor in tomato plants [130].

Mitigation of Abiotic Stress

Nano-clay use can help mitigate stress from salinity, drought, and heavy metals by adsorbing toxic ions and stabilizing soil pH [131]. Nano-clay treatment improved salinity tolerance in rice by reducing sodium uptake and improving potassium retention [132]. Integrating nano-clays in agriculture offers promising opportunities for improving plant growth and crop productivity,

particularly under stress conditions or in degraded soils. However, comprehensive long-term studies are needed to evaluate environmental impacts and optimize application methods.

NANOCLAYS IN ADVANCING AGRICULTURAL SUSTAINABILITY

Conceptual Framework

Sustainable agriculture refers to practices that meet current food production needs without compromising the ability of future generations to meet their own [133]. Traditional agricultural systems often suffer from inefficient nutrient use, waterscarcity, and excessive chemical inputs, leading to soil degradation and environmental pollution [134]. Nanoclays, including montmorillonite, kaolinite, bentonite, and halloysite, are emerging as natural, environmentally friendly materials with considerable potential to address these challenges [135]. Nanoclays possess high surface area, swelling capacity, cation exchange ability, and chemical stability, making them well suited for advancing agricultural sustainability through their capacity to function as carriers, slow-release agents, and soil conditioners [136].

Sustainability Benefits and Mechanisms

Nanoclays reduce reliance on chemical fertilizers and pesticides, thereby minimizing environmental pollution and supporting organic farming practices [137]. Their controlled-release properties substantially reduce the total amount of fertilizer needed, lowering production and application costs while improving environmental stewardship [143].

CHALLENGES AND FUTURE PROSPECTS

Current Limitations

Production Scalability and Cost

While nanoclay synthesis methods are established, scaling production to meet agricultural demand remains economically challenging. Current manufacturing costs limit widespread adoption, particularly in resource-limited agricultural regions [138].

Environmental Fate and Long-Term Effects

The long-term behavior of nanoclays in agroecosystems—including aggregation, sedimentation, or transformation—is not yet well understood [139]. Comprehensive long-term studies on nanoclay aging and transformation in

agricultural systems are needed [140].

Multidisciplinary Collaboration Gaps

Agronomic nanoclay research remains somewhat fragmented, with insufficient collaboration between soil scientists, toxicologists, material engineers, and policymakers [141]. Bridging these disciplinary gaps is essential for transitioning from laboratory innovations to field-ready solutions.

Future Opportunities and Directions Smart Delivery Systems

Emerging research focuses on stimuliresponsive systems capable of releasing nutrients or pesticides in response to environmental triggers such as moisture, pH, or temperature [148]. Biopolymer-coated halloysite nanoclay systems have demonstrated urea release in response to soil moisture, reducing nitrogen losses by up to 30% [142].

Hybrid Nanocomposites for Enhanced Functionality
Combining nanoclays with biochar,
biodegradable polymers, or bioactive molecules
can enhance performance and environmental
compatibility [143]. Nanoclay-biochar composites
have demonstrated improved water retention and
reduced pesticide runoff in arid soils [144].

Climate-Resilient Agricultural Applications

Nanoclays can address climate change impacts including water stress and nutrient leaching [145]. Their water-holding capacity and fertilizer release regulation prove particularly valuable in drought-prone regions [146]. Nanoclay-treated soils maintained higher moisture levels under prolonged dry conditions relative to untreated controls [147].

Integration with Precision Agriculture

Integration of nanoclays with remote sensing and Internet of Things (IoT) systems enables monitoring and controlled application, ensuring site-specific utilization and minimizing environmental impacts [148]. GPS-guided nanoclay delivery systems have been env.

CONCLUSION

Nanoclays represent a promising frontier in sustainable agriculture, offering innovative



solutions to address critical challenges in modern farming practices. Their unique physicochemical including high surface properties, layered structure, ion exchange capacity, and biocompatibility, make them ideal candidates for diverse agricultural applications. These materials enable controlled release of fertilizers and pesticides, significantly reducing chemical usage while enhancing nutrient bioavailability and minimizing environmental contamination. Additionally, nanoclays contribute substantially to soil remediation by immobilizing heavy metals and toxic substances, thereby restoring degraded agricultural lands. Their capacity to improve water retention in soil proves particularly valuable in drought-prone regions. Furthermore, nanoclays serve as effective carriers for biostimulants, promoting plant growth under stressful environmental conditions and helping farmers adapt to climate change impacts. These applications align directly with global sustainability goals, particularly those addressing food security, responsible production, and terrestrial ecosystem protection. However, realizing the full potential of nanoclay technologies requires addressing several challenges, including production scalability, cost reduction, comprehensive environmental impact assessments, and regulatory framework development. Successful implementation also demands interdisciplinary collaboration among scientists, policymakers, and agricultural stakeholders, alongside effective communication about benefits and risks. With continued research and responsible deployment, nanoclays are positioned to transform agriculture into a more sustainable, efficient, and resilient sector capable of meeting present and future global food demands.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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