Acta Scientific AGRICULTURE (ISSN: 2581-365X)

Volume 7 Issue 11 November 2023

Review Article

Clay Mineral Nanotechnology: Innovation in Agriculture

Prasad B Margal[1]*, Aniket S Gaikwad[1], Bhimrao M Kamble[2] and Nihal S Titirmare[1]

[1]Ph.D. Research Scholar, Department of Soil Science and Agricultural Chemistry, Post Graduate Institute, Mahatma Phule Krishi Vidyapeeth, Rahuri, Maharashtra, India

[2]Head, Department of Soil Science and Agricultural Chemistry, Post Graduate Institute, Mahatma Phule Krishi Vidyapeeth, Rahuri, Maharashtra, India

***Corresponding Author:** Prasad B Margal, Ph.D. Research Scholar, Department of Soil Science and Agricultural Chemistry, Post Graduate Institute, Mahatma Phule Krishi Vidyapeeth, Rahuri, Maharashtra, India.

DOI: 10.31080/ASAG.2023.07.1314

Received: July 11, 2023

Published: October 20, 2023

Abstract

Clay refers to soil particles with a size smaller than 2 µm. Clay minerals, due to their small size and large surface area, are considered naturally occurring nanomaterials capable of reacting with other molecules to achieve thermodynamic equilibrium. Clay nanotechnology involves the utilization of clay minerals to create materials with unique properties and applications. Polymer performance can be modified by incorporating various types of nanoparticles such as nanocarbons, carbon nanotubes, nano-clays, and metal oxides. The increased commercial interest and use of clay nanocomposites demonstrate the growing enthusiasm for employing nano-clays to modify polymeric materials for various applications. Nano-composites come in different types including bio, carbon, metal, clay mineral, exfoliated, intercalated, and polymer-based composites. Wet chemical methods, specifically the sol-gel technique, are employed to prepare nano clays. Clay mineral nanotechnology plays a significant role in crop protection, soil remediation, and improving crop and soil quality. It is also utilized in the development of nano fertilizers, pesticides, and herbicides for sustainable agriculture.

Keywords: Clay; Mineral Nanotechnology; Agriculture

Introduction

Clay minerals refer to soil particles that are less than 2 µm in size and have sheet-like structures composed of hydrous aluminum or magnesium silicates [1]. There are two main types of clay minerals: (i) residual clay, which is formed through weathering of rocks or shale (compressed clay, silt, or mud in a fine-grained sedimentary rock) and found in the place of origin, and (ii) transported clay (or sedimentary clay), which is eroded from its original location and deposited elsewhere. Due to their small size and large surface area, clay minerals are considered a naturally occurring nanomaterial that can react with other molecules to attain thermodynamic equilibrium [2].

Clay mineral nanotechnology is a branch of nanotechnology that utilizes clay minerals to develop materials with novel properties and applications. Clay minerals possess unique physicochemical and structural properties that make them ideal for use in various industrial and agricultural applications. In agriculture, clay mineral nanotechnology has the potential to enhance soil fertility, increase nutrient uptake and water retention and improve plant growth. Clay mineral nanotechnology uses tiny clay nanoparticles for agricultural applications. By applying these nanoparticles to the soil, farmers can reduce the use of chemical fertilizers and pesticides. They can also be used in packaging, smart sensors, and other areas of agriculture. This technology offers a sustainable and eco-friendly approach to enhancing crop productivity and food security.

Nano-clay

Nano-clays are made up of thin layers, with each layer having a thickness of one to a few nanometers and a length ranging from

Properties	Kaolinite	Illite	Montmorillonite	Vermiculite	Chlorite
Size (microns)	0.1-5.0	0.1-2.0	0.01-1.0	0.1-0.5	0.1-2.0
Shape	Hexagonal	Irregular flakes	Irregular flakes	Plates and flakes	Variables
C- axis spacing (A^0)	7.2	10	14	10-15	14
CEC (c mol kg^{-1})	3-15	15-20	80-100	80-150	10-40
AEC (c mol kg^{-1})	43	-	≤ 5	-	-
Internal surface area ($m^2 g^{-1}$)	7-10	70-100	500-600	700-800	60-80
External surface area ($m^2 g^{-1}$)	30-35	50-70	80-150	80-100	70-100

Table 1: Properties of phyllosilicate clay minerals.

Source: A Textbook of Pedology: Concepts and Applications by J Sehgal.

Nutrient	Minerals
P	Apatite $Ca_5(PO_4)$, Francolite $[(Ca, Mg, Sr, Na)_{10}(PO_4, SO_4, CO_3)_6F_2]$
K	Kainite (KMg (SO_4) $Cl_2.75H_2O$), Orthaclase ($KAlSi_3O_8$), Sylvite (KCL)
Ca	Calcite ($CaCO_3$), Dolomite (CaMg $(CO_3)_2$), Anorthite ($CaAl_2Si_2O_8$)
Mg	Dolomite (CaMg $(CO_3)_2$), Olivine ($(Mg, Fe)_2SiO_4$), Biotite
Zn	Sphalerite (ZnS), Smithsonite ($ZnCO_3$), Hemimorphite [Zn_4 (OH_2) $Si_2O_2H_2O$]
Cu	Chalcocite (Cu_2S), Covellite (CuS), Malachite, Azurite, Chrysocolla
Fe	Hematite (Fe_2O_3), Goethite (FeOOH), Magneite (Fe_3O_4), Pyrite (FeS_2), Olivine
Mn	Pyrolusite (MnO_2), Manganite (MnOOH), Rhodochrosite ($MnCO_3$), Rhodonite
B	Borax, Kernite, Colemanite, Kotoite, Tourmaline
Mo	Molybdenite (MoS_2), Wulfenite ($PbMoO_4$), Ferrimolybdite, Powellite
Cl	Sylvite (KCL), Sodium Chloride (NaCl)
Ni	Olivine, Serpentine

Table 2: Sources of nutrients.

Source: A Textbook of Pedology: Concepts and Applications by J Sehgal.

a few hundred to several thousand nanometers. Due to their ability to provide various desired effects, nanoparticles are now being used as fillers or additives in polymers, and they are receiving increasing attention in research and development. Nanocarbons, carbon nanotubes, nano-clays, and metal oxides are some of the various types of nanoparticles currently utilized to modify polymer performance. The growing interest in the use of nano-clays for modifying polymeric materials for a range of applications is evidenced by increased commercial interest and consumption of clay nanocomposites, which constituted almost one-quarter (24%) of the total nano-composites consumed in 2005 [3].

Types of nano-composites

Nano-composites are materials composed of two or more different components with at least one of them in the nanoscale range. There are several types of nano-composites based on the type of nanomaterial used and the method of preparation. Some of the most common types of nano-composites include:

- **Bio-based nano-composites** are made by incorporating nanoparticles into a biopolymer matrix, resulting in materials with improved biodegradability, biocompatibility, and bioactivity. They are used in various applications, such as in tissue engineering, drug delivery and food packaging.
- **Carbon-based nano-composites** such as carbon nanotubes and graphene, have been used in agriculture for various applications, including sensors for detecting soil moisture and nutrient levels, and as carriers for delivering plant growth regulators.
- **Clay mineral-based nano-composites** these include montmorillonite, halloysite and other clay minerals that have been modified with polymers or other nanoparticles. They are used as fillers in various agricultural materials

such as packaging films, mulch films, and biodegradable nanocomposites.

- **Exfoliated nano-composites** are produced when polymers penetrate deeply into the clay layers, causing them to separate and scatter randomly throughout the polymer matrix. This type of composite is considered the most effective due to the excellent interaction between the polymer and clay, resulting in superior properties.
- Intercalated nano-composites are formed when polymer chains penetrate into the interlayer space of clay, leading to the formation of a well-ordered structure consisting of multiple layers of alternating polymer and inorganic layers. This arrangement repeats itself at a distance of a few nanometers.
- Lipid-based nano-composites such as nano emulsions, have been used in agriculture as delivery systems for plant growth regulators and pesticides.
- Metal-based nano-composites such as silver nanoparticles, are used as antimicrobial agents in various agricultural materials such as packaging films, coatings and seed treatments.
- Polymer-based nano-composites are composites in which a polymer matrix is reinforced with nanoparticles, such as clay, carbon nanotubes, or graphene.

Methods and process of preparation of nano clay

The sol-gel technique is a wet-chemical method that has gained popularity in the fields of ceramic engineering and materials science [4]. It is a bottom-up approach that involves the creation of a network of particles or nano composites from a chemical solution precursor. The precursors used are typically acetic, nitric, chloride, formic, or sulphuric acids, which undergo various forms of reactions. The sol gradually evolves into a gel-like biphasic system that contains both a solid and liquid phase, with morphologies ranging from individual particles to continuous networks. In this process, sodium clay powders (1.16g) are dissolved in de-ionized water and citric acid (0.38g) is added. The mixture is stirred using a magnetic stirrer while ammonium hydroxide is added to adjust the pH to 7. The mixture is then heated in a furnace at 100°C for 20 hours, resulting in the formation of a powder after initially forming a gel.

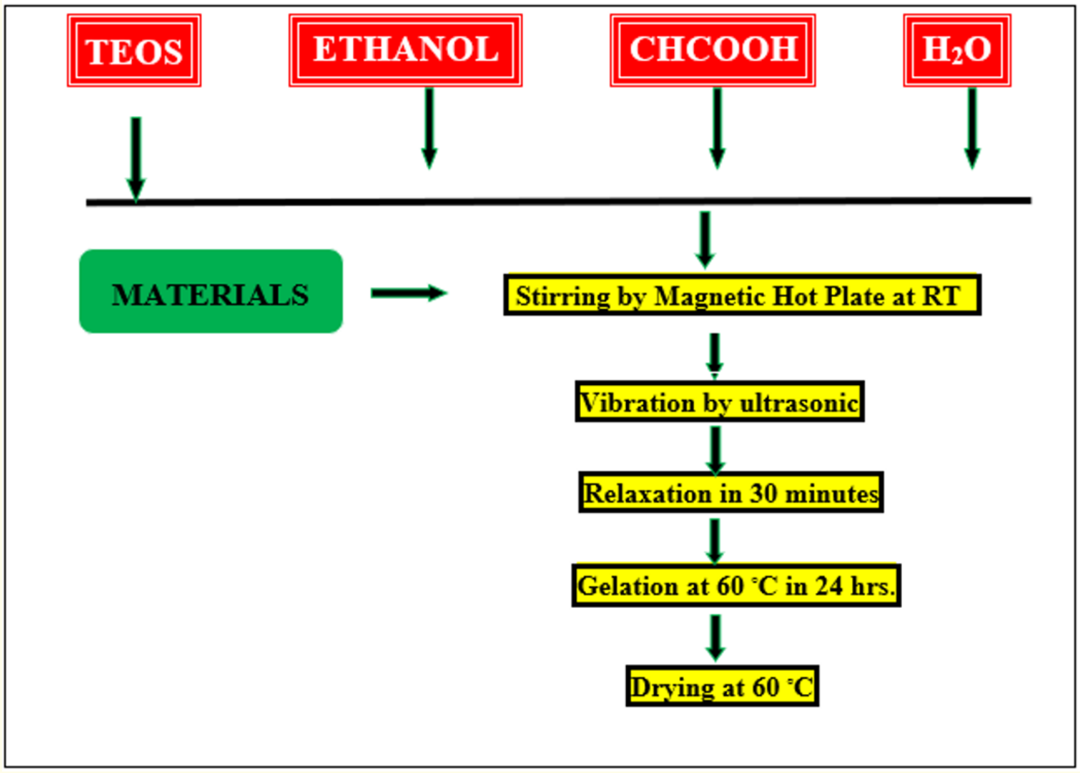

Figure 1

Importance of clay minerals nanotechnology in agriculture

- **Cost effective:** The use of clay minerals in agriculture can be cost-effective due to their abundance, low cost, and wide availability in various regions of the world.
- **Crop protection:** Clay minerals can be used to create nanostructured materials with antibacterial and antifungal properties to protect crops from pests and diseases. They can also create films that protect crops from UV radiation.
- **Improved crop quality:** By improving soil fertility and nutrient uptake, clay minerals can improve the quality of crops, making them more nutritious and visually appealing.
- **Improved livelihood:** Improved crop yields resulting from the use of clay minerals in agriculture can lead to increased income and improved livelihoods for farmers, especially in developing countries.
- **Nano fertilizers:** Clay minerals can be used as a carrier material for nanoparticles that can enhance the efficiency of fertilizers by improving nutrient uptake by plants.
- **Soil improvement:** Clay minerals can improve soil structure, water retention, and nutrient availability, which can result in increased crop yields and reduced need for irrigation and fertilizers.
- **Soil remediation:** Clay minerals can be used to remove contaminants from soil through a process called adsorption. The high surface area of clay minerals allows them to bind with heavy metals and other pollutants, removing them from the soil and preventing them from entering the food chain.
- **Sustainable agriculture:** The use of clay minerals in agriculture can promote sustainable practices by reducing the need for harmful chemicals and fertilizers that can harm the environment and human health.
- **Water conservation:** Clay minerals can improve water retention in soil, reducing the need for frequent irrigation. This can be particularly important in areas with limited water resources or where drought is a common problem.

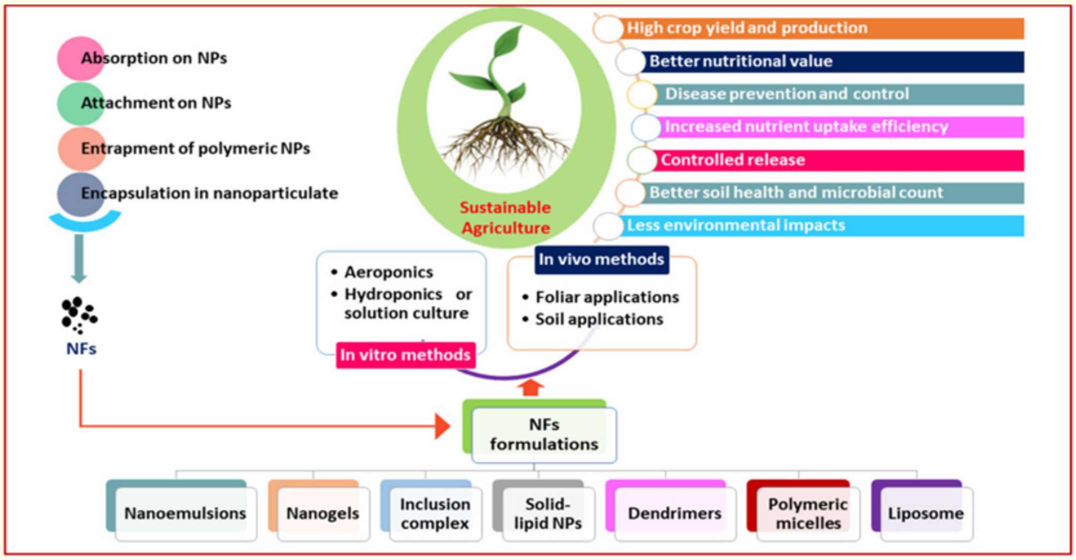

Figure 2

Applications of clay minerals nanotechnology in agriculture

- One of the potential applications of nano-clay in agriculture is as a carrier for controlled-release fertilizers. Nanoclay can effectively adsorb and release nutrients over a prolonged period of time, which can reduce the leaching of nutrients into groundwater and improve the efficiency of fertilizer use.
- Clay mineral nanotechnology can improve crop protection against pests and diseases by creating nanostructured materials with antibacterial and antifungal properties. Clay minerals can also be used to create films that protect crops from UV radiation.

- Clay mineral nanotechnology has potential in developing nano fertilizers. Clay minerals can act as a carrier for nanoparticles, which enhances nutrient release and uptake by plants. Montmorillonite clay has been used as a carrier for zinc nanoparticles to improve the growth and yield of rice plants in India.

- Clay minerals, like montmorillonite, can enhance soil fertility by having a high cation exchange capacity (CEC) to attract and retain positively charged ions viz., K, Ca and Mg. Incorporating clay minerals in soil can improve nutrient availability to plants and increase yield. For instance, in Nigeria, applying montmorillonite clay to soil resulted in improved growth and yield of tomato plants.

- In addition, nano-clay can be used as a carrier for pesticides and herbicides, which can reduce their environmental impact and improve their efficacy.

- Nano clay particles have been used to develop a clay-based pesticide formulation for controlling plant parasitic nematodes. This formulation is more effective than conventional nematicides and uses nano clay particles to deliver a nematicide to plant roots, reducing the damage caused by nematodes and improving crop yields. Researchers at the University of California, Riverside, developed this environmentally friendly formulation.
- Nano-clay has also shown potential for use in soil remediation, particularly for the removal of heavy metals and organic contaminants from contaminated soils.
- Nano-clay particles can adsorb contaminants onto their surfaces, which can facilitate their removal from the soil. In summary, nano-clay is a promising material for improving soil quality and enhancing crop productivity in agriculture.

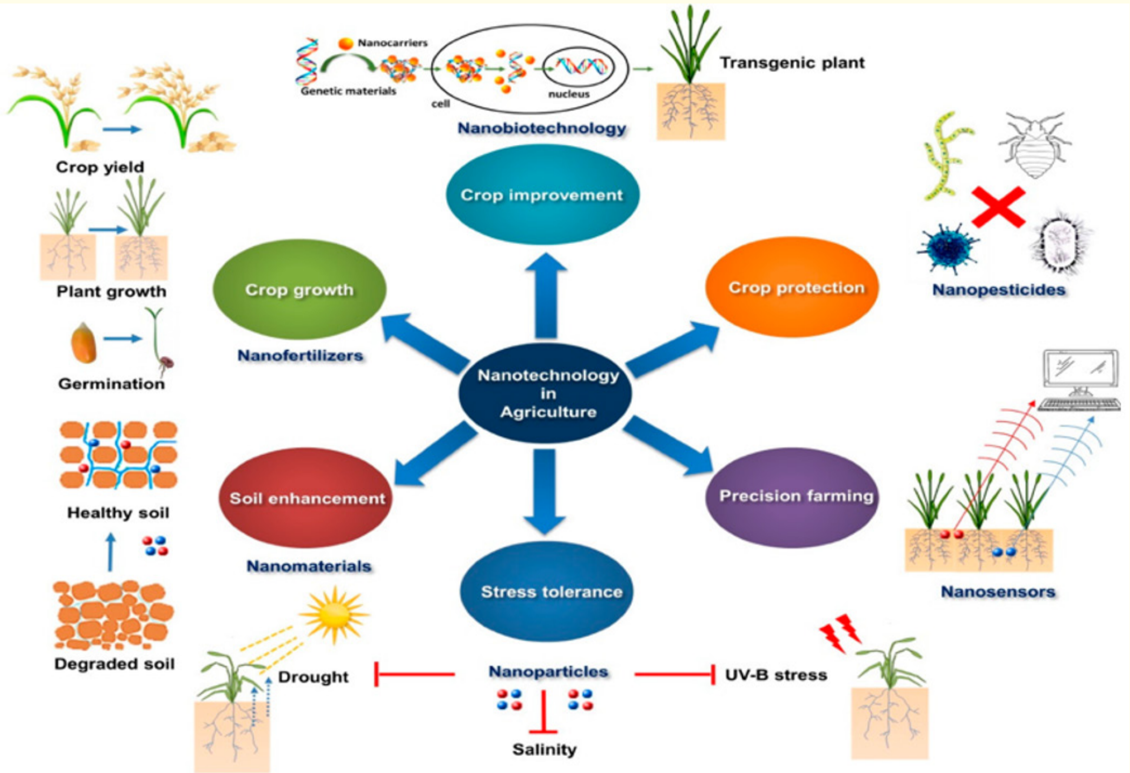

Figure 3

Conclusion

Clay mineral nanotechnology is a promising field with numerous potential applications in agriculture, such as soil conditioning, fertilizer carriers, and crop protection. It has the potential to enhance soil fertility, water retention, and nutrient uptake, leading to increased crop yields with reduced environmental impact and improved soil and plant health. Its unique physicochemical properties make it ideal for various applications, including controlled-release fertilizers, soil remediation, and pesticide and herbicide carriers. Ongoing research and development in this area may lead to further innovations in sustainable agriculture and environmental management.

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