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A Review on Hydroxyapatite: Properties, Its Composite, and Its Slow-Release Fertilizers Application

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Abstract

Hydroxyapatite (HAp), a natural mineral form of calcium apatite, has recently received significant attention due to its potential application as a slow-release fertilizer. This review aims to comprehensively analyze HA and its composites, focusing on properties, synthesis methods, and nutrient release mechanisms in agricultural applications. HA's high biocompatibility, excellent adsorption capacity, and ability to release nutrients gradually make it an ideal candidate for increasing soil fertility and crop yields. This review also explores the incorporation of other materials, such as urea, carboxylated cellulose, and montmorillonite, to form HA composites, thereby increasing their efficiency as fertilizer. In addition, the environmental benefits of using HA-based fertilizers, such as reduced nutrient leaching and improved soil health, were also investigated. Challenges and future perspectives are also discussed, emphasizing the need for further research to optimize these materials for practical agricultural use. This review highlights the potential of HA and its composites to revolutionize sustainable agriculture by providing a controlled and efficient nutrient release system.

Keywords: Composites, Hydroxyapatite, Slow-release fertilizer

1 Introduction

Technological developments in agriculture, particularly in fertilizer application, have become imperative due to the growing global demand for food. Conventional fertilizers, such as urea, nitrogen, phosphorus, potassium, monoammonium phosphate, and diammonium phosphate, are widely used to supplement essential nutrients in the soil [1]. However, most of the time, the active ingredients in conventional fertilizers degrade (chemically, photochemically, and biologically), leach, discharge, volatilize, are absorb, or become immobilized in the soil before significant plant uptake occurs. Soil fertility decreases significantly as a result of the buildup of layers of soil. This is mainly because conventional fertilizers have a relatively poor nutrient utilization efficiency of around 30-35% for nitrogen, 18-20% for phosphorus, and 35-40% for potassium [2]. Therefore, the need for more effective and environmentally benign fertilizers arises from the harm caused by excess nutrients released into the environment.

Different techniques can be used to address these slow delivery of nutrients from fertilizers to plants; the resulting products are referred to as slow-release fertilizers (SRFs) [4]. SRFs are defined as low-solubility molecules with a complex or high molecular weight chemical structures that can be broken down chemically or by microbes to release nutrients [3]. Reducing the rate of nutrient release can mitigate nutrient loss and increase nutrient use efficiency (NUE) [4]. Among the various materials investigated for SRFs, hydroxyapatite has gained considerable attention due to its unique properties and potential benefits.

The naturally occurring mineral calcium apatite, hydroxyapatite (HAp), has attracted attention due to its potential use in slow-release fertilizers. Hydroxyapatite nanoparticles, with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, can serve as a sustainable source of calcium and phosphate micronutrients. They can also be utilized in surface modification for the formation of nanohybrids [5]. Due to its form, hydroxyapatite is extensively used in both biomedical and agricultural fields because of its remarkable stability and compatibility with living organisms [6–8]. These properties make it an ideal candidate for use in agricultural systems aimed at improving sustainability and efficiency. The agricultural objective of this review is to explore the potential of hydroxyapatite. Its primary objective is to explore hydroxyapatite's potential properties, synthesis methods, nutrient release mechanisms, and agriculture applications. By understanding the various aspects of HAp and its effectiveness as an SRF, this review aims to provide insights into its advantages, challenges, and prospects in sustainable agriculture. The findings and insights presented here are expected to serve as a valuable resource for researchers, farmers, and policymakers interested in enhancing agricultural productivity while minimizing environmental impacts.

2 Hydroxyapatite Properties

Hydroxyapatite (HAp) is an inorganic compound with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, arranged in a crystal structure similar to the main minerals found in bones and teeth. Generally, HAp has a hexagonal structure with a relative molecular mass (Mr) of 502.31 g/mol [11,58]. The composition of HAp consists of calcium phosphate-containing hydroxide with an ideal Ca/P molar ratio of 1,67 [9]. The composition of HAp consists of calcium phosphate-containing hydroxide with an ideal Ca/P molar ratio of 1,67 [9]. HAp is a bioceramic known for its favorable bioactivity, biocompatibility, and osteoconductive properties [10]. HAp can be sourced from natural materials as a source of calcium, such as coral, seaweed, and chicken eggshells [55-57]. Chicken eggshells are one of the natural materials that are easy to use, and currently, chicken eggshells represent a fairly serious waste problem.

The structure of HA consists of two forms, hexagonal and monoclinic, which appear in **Fig. 1.** HAp with a hexagonal structure has a P63/m space group with lattice parameters a=b= 9.432 Å, c = 6.881 Å, dan γ = 120°, while the monoclinic structure has a P21/b space group with lattice parameters a= 9.421 Å, b = 2a, c = 6.881 Å, dan γ = 120° [11]. HAp has two types of crystal planes with different total charges. The a and b planes are positively charged and attract negatively charged molecules, while the c plane is negatively charged and attracts positively charged molecules[12]. In addition, the three main components in HAp (Ca^{2+}, PO_4^{3-}, and OH^- groups) create unique characteristics that allow for substitution [13].

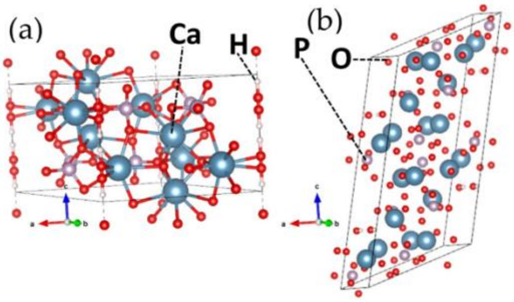

Figure 1. The crystal structure of HAp can be (a) hexagonal or (b) monoclinic, with the monoclinic structure having a c-axis longer than the a and b axes [14].

HAp can accommodate large amounts of anionic and cationic substituents, a superior characteristic for use in various applications [15]. The microstructure of HAp, including porosity, crystallinity, particle shape, size, and distribution, determines its effectiveness, providing flexibility to improve and modify the material properties based on the application [16].

The morphology and characteristics of HAp vary significantly, even though its basic structure remains identical regardless of the source or processing conditions. In addition to its original state, HAp can be substituted or functionalized both during and after synthesis to achieve the desired qualities for specific applications [17]. The most common methods used for the synthesis of HAp include the co-precipitation method [18–21], sol-gel synthesis [22–25], hydrothermal synthesis [18,26,27], and sonochemical methods [28–30]. Chemical synthesis allows greater control over the structure and characteristics of HAp. However, the technique, structure, and processability of HAp will be significantly affected by the chemicals and conditions used during its synthesis.

HAp has several physical properties that make it suitable for agricultural applications, one of which is its use as a fertilizer. HAp has low solubility and is commonly used as a phosphorus fertilizer. Consequently, there is a greater likelihood that phosphorus solubility can be enhanced by formulating nanoparticles [31]. Moreover, HAp can act as a carrier for various macro- and micronutrients, creating opportunities for the efficient and targeted delivery of multiple nutrients to plants [32].

HAp-based fertilizers employ several mechanisms to achieve slow nutrient release, ensuring a sustained supply of essential elements to plants while minimizing environmental losses. The lattice structure of HA is well known for its extraordinary capacity to hold nearly half of elements in the periodic table [33,34]. Along with Ca^{2+} and PO_4^{3-} ions, the OH^- ions in the HAp are arranged in columns parallel to the c-axis [35]. Adsorption mechanisms are supported by all of these ions/groups in different ways due to their unique features, such as flexible substitutability in HAp. Several researchers have reported that HAp undergoes adsorption through various mechanisms, including surface complexation, ion exchange reactions, partially soluble new phase deposition, and physical adsorption, such as hydrogen bonding and electrostatic interactions [36]. The gradual release of nutrients is facilitated by HAp's ability to exchange ions. Electrostatic forces hold nutritional ions that have been adsorbed onto HAp particles in place, allowing plants to progressively exchange them with other ions in the soil solution as needed.

3 Slow-Release Concept and Mechanism

Slow-Release Fertilizer (SRF) is a type of fertilizer designed to release nutrients gradually and in a controlled manner into the soil over a period. Unlike conventional fertilizers that dissolve quickly and release nutrients instantly, SRF minimizes nutrient losses due to leaching, volatilization, or denitrification, thereby increasing nutrient uptake efficiency by plants [37–41]. The main purpose of developing slow-release fertilizers is to improve the quality of conventional fertilizers and to reduce environmental hazards and resource waste. A good slow-release fertilizer has an environmentally safe and biodegradable layer of organic or inorganic polymeric materials that slows its release, enabling it to meet the mineral requirements for plant growth [54].

Slow-release fertilizers are classified into three types: physical type, chemical type, and compound type as shown in **Fig. 2.** The physical type is a fertilizer that can overcome the shortcomings of rapid fertilizer dissolution into the soil but cannot control the soil transformation behavior of the dissolved fertilizer. This physical type is divided into layered fertilizers and matrix fertilizers. The chemical type is a fertilizer that can slow down the enzymatic hydrolysis rate, although the delayed hydrolysis time is short, and can be affected by soil type and crop variety. Chemical type SRF can be divided into chemically bound fertilizers and chemically inhibited fertilizers. The compound type is a fertilizer that can more effectively control the dissolution and transformation process of fertilizers in the soil [31].

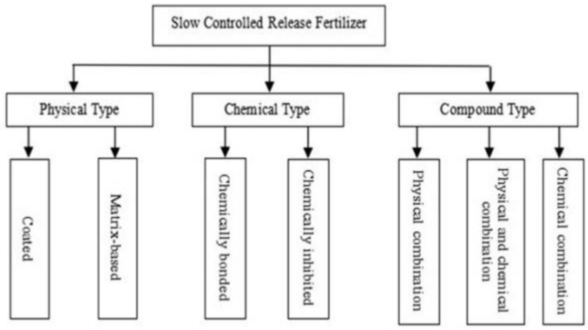

Figure 2. Classification of slow-release fertilizers [31]

The nutrient release mechanism in slow-release fertilizers (SRF) is generally divided into three main types: coated, biological, and chemical systems. In coated systems, nutrient release is regulated by diffusion, dissolution, and degradation of the polymer membrane that encapsulates the nutrients. Biological systems rely on microbial activity in the soil to degrade the fertilizer matrix, while chemical systems are influenced by environmental factors such as soil pH and moisture content, as observed in ammonium urate-based fertilizers [42].

Although mathematical models have been developed to predict nutrient release behavior, many still oversimplify the process and fail to consider key environmental variables, making them less effective in real agricultural conditions. Furthermore, most models focus on single-nutrient fertilizers (e.g., N, P, or K), highlighting the need for more comprehensive approaches for multi-nutrient formulations. Since much of the current research is conducted under laboratory conditions, the performance of SRFs/CRFs in actual field environments can vary significantly. Therefore, integrating digital agriculture technologies such as the Internet of Things (IoT), big data analytics, and real-time soil sensors is essential to monitor nutrient demand accurately and adjust release rates accordingly, enhancing efficiency and supporting sustainable agricultural practices [43].

4 Slow-Release Fertilizer by HAp and Its Composite

HAp composite is defined as HAp mixed with another substance to improve its properties. Many experiments have been conducted recently to improve the physicochemical and mechanical properties of HAp [44]. Several studies report the combination of HAp with urea, one of the most widely used nitrogen fertilizers, to form composites that offer a more sustainable approach to nutrient management in agriculture. This detailed explanation explores the properties, synthesis, benefits, and challenges associated with HAp-Urea composites as slow-release fertilizers.

Previous research has explored the development of environmentally friendly nanoparticles carrying urea as a slow-release plant nutrient, with a focus on its application in agriculture [31]. Urea is incorporated into hydroxyapatite nanoparticles, known for their biocompatibility and phosphorus-rich properties, to create nanohybrids that provide a platform for slow release. The synthesis of these nanohybrids involves a one-step *in situ* approach. The results indicate that urea is weekly bound to the nanoparticles, leading to a slow and sustained release of nitrogen. This slow release was confirmed through water release tests, which showed that the nitrogen release rate of the HAp-urea nanohybrids was reduced by approximately 12-fold compared to that of pure urea, showcasing the potential of these slow-release fertilizers to optimize nutrient delivery in agriculture [31]. Similar studies have also reported that the slow-release function of hydroxyapatite is achieved through mechanisms such as hydrogen bonding between urea molecules and the surface functional groups of the carrier, as well as the binding interactions between calcium and nitrogen atoms. The research results on urea release by hydroxyapatite show that HA-urea nanohybrids can reduce urea release by 11.5 times compared to pure urea [45]. Several studies on hydroxyapatite and urea nanohybrids are presented in **Table 1.**

Table 1. Recent application and performance of Hydroxyapatite (HA) as Slow-Release Fertilizers (SRFs)

Release Study	Synthesis Method	Shape	Sources
The urea-hydroxyapatite nanohybrids exhibit a slow and sustained release of nitrogen, with a release rate that is 12 times slower than that of pure urea	One-step *in situ* coating approach	Rod	[31]
Applying hybrid fertilizer affected the growth and yield of the *Capsicum* annuum pepper plant by enhancing plant height by up to 150%, stem diameter by up to 168%, number of leaves by up to 167%, and number of fruits up to 449%, fruit diameter up to 200% and fruit weight up to 234%, compared with the unfertilized plant.	Wet chemical precipitation method	-	[46]
Ur@HANP exhibited sustained release of urea, leading to enhanced crop growth in rice seed germination experiments. The slow release of nitrogen from Ur@HANP was evidenced by lower nitrate and ammonia concentrations in the leachate compared to urea and phosphate treatments.	Sol-gel method	-	[47]
The study demonstrated that the urea release from the hydroxyapatite nanohybrids was significantly slower compared to uncoated urea, with the rate of urea release being 11.5 times slower in the nanohybrids	One-step *in situ* coating approach	Rod	[45]
The release study results indicated that the NH_4-N concentration in the drainage was reduced by 10.6% in the urea-doped hydroxyapatite nanomaterials (UHN) at recommended (UHN_RD) and by 16.3% in the lf-recommended (UHN_HRD) treatment compared to the commercial bulk urea fertilizer (BUF) treatment.	Sol-gel method	Rod	[48]
The hydroxyapatite-urea nanohybrids in Low Country and Uva showed yield increases of 10–17% and 14–16%, respectively, compared to conventional recommendations.	One-step *in situ* coating approach	Rod	[49]
Urea-doped nanohydroxyapatite enhances nutrient release efficiency and maintains crop yield and quality, even with reduced fertilizer application rates, offering a promising alternative to conventional fertilizers	Chemical precipitation	Rod	[50]
Hydroxyapatite-urea nanohybrids significantly improve nitrogen utilization efficiency, resulting in a ~69% increase in crop yields and enhanced plant growth in rice compared to standard nitrogen applications in pot trials.	Mechanochemical synthesis	Coral	[51]

5 Limitations and Future Perspectives

The primary challenge of using hydroxyapatite (HAp) and its composites as slow-release fertilizers (SRFs) is the high cost of production, driven by complex and costly synthesis processes and the difficulty in scaling up to meet agricultural demands. Regulatory hurdles and market acceptance pose further challenges, as introducing new fertilizer products requires rigorous testing and approval. Moreover, convincing farmers to adopt these fertilizers necessitates demonstrating clear economic and agronomic benefits.

To address these challenges, research into more cost-effective synthesis methods and the recycling of HA from industrial by-products could help reduce production costs. Comprehensive field trials across diverse crops, soil types, and climatic conditions, along with long-term studies, are essential for understanding the cumulative effects on soil health and crop productivity. Educating farmers through outreach programs and and demonstration projects can facilitate the adoption of HAp-based SRFs. By addressing these limitations and leveraging future research opportunities, HAp and its composites have the potential to advance sustainable agriculture and improve nutrient management practices significantly.

6 Conclusion

Hydroxyapatite (HAp) and its composites are promising materials for slow-release fertilizers (SRFS), offering benefits such as improved nutrient use efficiency, reduced environmental impact, and enhanced soil health. They release nutrients gradually, aligning with plant uptake and minimizing the need for frequent fertilization. This controlled release helps protect water bodies from eutrophication and reduces greenhouse gas emissions. Additionally, HAp improves soil structure, water retention, and microbial activity.
However, challenges include high production costs, scaling issues, achieving uniform field distribution, and potential long-term environmental impacts. Future research should focus on cost-effective synthesis methods, recycling HAp, developing multi-nutrient composites, and conducting extensive field trials. Educating farmers through outreach programs and streamlining regulatory approval processes are also essential. Addressing these challenges and leveraging research opportunities can significantly advance sustainable agriculture, improve nutrient management practices, and contribute to global food security and environmental sustainability.

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