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Performance and challenges of hydroxyapatite and its nanocomposite-based nanofertilizers: A review

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ABSTRACT

The potential of hydroxyapatite (HA) nanoparticles as an alternative fertilizer has been extensively explored to mitigate the negative effects of conventional fertilizers on soil health. However, their low solubility in soil remains a significant challenge as this property reduces their efficiency for controlled nutrient delivery. To address this challenge, organic-inorganic nanocomposites, particularly HA-biopolymer-based nanofertilizers, have been proposed. These biocomposites combine the nutrient-rich feature of HA with the improved solubility and controlled-release ability provided by biopolymers, while also enhancing soil interaction to ensure more efficient and sustainable fertilization. The polymeric phase plays a key role in nutrient solubilization kinetics by facilitating microbial release, minimizing the need for frequent application, and reducing the toxicity to plants, which altogether reduces the overall environmental implications of fertilizer application. Despite recent advances, several key scientific gaps remain unaddressed, including the optimization of synthesis methods, the role of polymer composition in nutrient release kinetics, and the long-term effects of these nanofertilizers on soil health and plant productivity. This review provides a comprehensive analysis of the recent progress and prospects for HA-based nanofertilizers, emphasizing synthesis techniques, structural properties, and performance in soil environments. Additionally, it highlights the need for tailored approaches to optimize nutrient release profiles, ensuring sustained nutrient availability, reduced environmental impact, and enhanced agricultural productivity. By identifying these knowledge gaps, this review aims to guide future research toward the design of next-generation HA-biopolymer nanocomposites with improved efficiency and sustainability compared to existing ones.

Key Words: biocomposite, biopolymer, CaP material, organic-inorganic nanocomposite, slow controlled-release fertilizer

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INTRODUCTION

The current food crisis remains one of the most pressing global challenges of our time, driven by rapid population growth and increasing food demand (Chen *et al*., 2018). Fertilizers are used around the world to help farmers boost their productivity, which has led to a rise in fertilizer demand from 46.8, 43, and 172.2 Mt in 2018 to 50, 45, and 183.3 Mt in 2023 for phosphorus (P), potassium (K), and nitrogen (N), respectively (Sim *et al*., 2021). This increase in demand is due to the additional production expenses associated with each cycle's additional supply of fertilizers and the low nutrient use efficiency (NUE) of conventional fertilizers (CFs), which range from 10%–25% for P to 50%–60% for N and K fertilizers (Bi *et al*., 2020; Sim *et al*., 2021). The unused portion of these nutrients is lost through processes such as volatilization, denitrification, runoff, and leaching (Stanley and Mahanty, 2020). The low NUE increases the amount of fertilizers needed, thereby increasing the costs of crop fertilization (Vishwakarma *et al*., 2018). Therefore, there is an urgent need for precision fertilizers that can provide sustained nutrient release.

Recently, several research studies on slow/controlled-release fertilizers (SCRFs) have shown promise in improving nutrient uptake efficiency by regulating solubility or prolonging nutrient availability (Eghbali *et al*., 2015). Nanoscale structures such as nanoclays, carbon-based nanomaterials, calcium phosphate (CaP) nanoparticles, polymer-based nanocomposites, and mesoporous silica superabsorbent hydrogel-based fertilizers are regarded as promising potential candidates to design novel SCRFs with higher NUE, which will enable more sustainable agriculture practices and improved plant productivity (Guo *et al*., 2018).

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The CaP nanomaterials, especially hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), have emerged as a promising solution to improve the P use efficiency of CFs (Maghsoodi *et al*., 2020). When used for the design of P nanofertilizers, HA can reduce nutrient leaching and improve P uptake by plants (Maghsoodi *et al*., 2020; Elsayed *et al*., 2022). The potential of using this low-cost and widely available form of P to achieve slow/controlled-release properties has triggered interest from researchers to improve the performance of HA through a variety of HA-based fertilizer formulations. For example, nanoparticles of HA were introduced as a source of P to improve crop nutrition and soil interaction (Fellet *et al*., 2021). Combining HA with polymeric materials is another possible solution to enhance the controlled-release ability of fertilizers (Giroto *et al*., 2017; Elhassani *et al*., 2019; Rop *et al*., 2020). However, the development of HA-based fertilizers is still in its exploratory phase, and several critical parameters must be addressed to fully enable their applicability in the field. These include optimizing the synthesis techniques, understanding their physicochemical properties, and evaluating their nutrient release behavior and impact on soil properties.

This review provides a critical analysis of HA-based nanofertilizers, including doped HA structures and HA-polymer composites, as innovative solutions for sustainable P management. It discusses the different synthesis techniques, nutrient release kinetics, and the impact of HA-based SCRFs on soil properties and plant growth metrics. Additionally, this review highlights recent advancements in HA-based composite fertilizers and identifies key knowledge gaps that must be addressed to improve their efficiency and field applicability.

SCRFS

In recent years, several formulations of SCRFs have been developed. The classification of SCRFs depends on the preparation technique and the encapsulating or coating compound used. The encapsulating/coating substrate provides SCRFs a physical barrier to control the release of nutrients from the carrier matrix (Bley *et al*., 2017). There are three main categories of SCRFs: i) natural organic materials (wastewater sludge, animal waste, *etc*.) and synthetic low-solubility organic materials, ii) water-soluble fertilizers with physical barriers (organic or inorganic) to control nutrient release (Mansouri *et al*., 2023), and iii) inorganic low-solubility substances, including HA, ammonium potassium phosphate, magnesium ammonium phosphate, and partly acidulated phosphate rock (PHR) (Shaviv, 2001; Trenkel, 2010) (Fig. 1).

Inorganic mineral-based SCRFs

Inorganic materials like bentonite, diatomite, dolomite, gypsum, sulfur (S), and zeolites are widely employed as coating agents in the manufacturing of SCRFs (Dubey and Mailapalli, 2019). These materials play a crucial role as diffusion barriers, thus controlling the nutrient release from the fertilizer. The efficiency of the coating materials can be affected by several parameters like thermal stability, coating thickness, chemical structure, and water uptake property (Shaviv, 2001). An ideal controlled-release fertilizer is generally covered with biodegradable compounds that provide controlled release of nutrients under different conditions. Moreover, the nutrient release profile should be similar to the nutrient absorption curve of the plant to maximize its uptake and reduce losses (Guelfi *et al*., 2022). A slow-release inorganic fertilizer consisting of chitosan polymer and oleic acid-coated struvite-K particles was developed by Atalay *et al*. (2022), and the release of K, P, and magnesium (Mg) was studied as a function of time and pH. The results revealed a sustained release of nutrients over 10 d of the experiment. Many studies have also reported the use of elemental S as a coating agent, despite its oxidation in the presence of soil microorganisms (Liu *et al*., 2008; Mehmood *et al*., 2019; Valle *et al*., 2022). Fertilizers based on polysulfide with

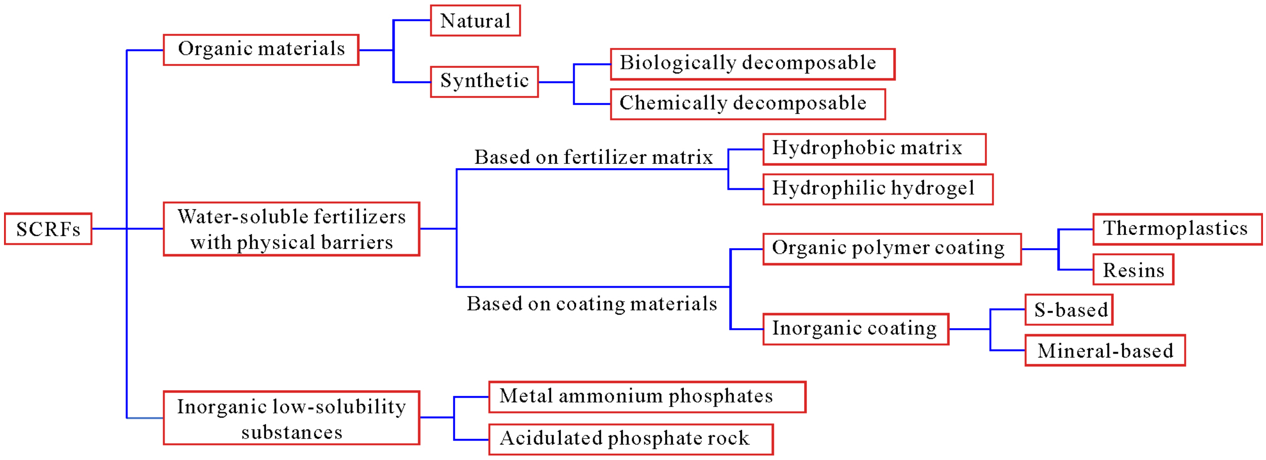

Fig. 1 Categories of slow/controlled-release fertilizers (SCRFs).

dispersed struvite were investigated for soybean nutrition due to their controlled-release properties (Valle *et al.*, 2022). Superior biomass was noted for polysulfide-struvite composite compared to triple superphosphate (TSP) combined with ammonium sulfate. For the polysulfide-struvite composite treatment, the biomasses of shoots and roots were 3 and 10 times, respectively, higher compared to TSP combined with ammonium sulfate. A higher proliferation of second-order lateral roots was also noted in response to struvite ongoing P delivery, while P uptake efficiency (11%–14%) was similar for the treatments. Bioactive S-coated diammonium phosphate (DAP) was used to enhance N and P use efficiencies by maize. Statistical analysis demonstrated that the maximum improvement was observed with the use of 8% S-coated DAP, which enhanced plant height (39%), chlorophyll content (21%), kernel yield (79%), 1 000-grain weight (27%), and N (56%) and P (52%) concentrations compared to the uncoated DAP control (Sattar *et al.*, 2021). A composite based on a matrix of zero-valent S (S^0) and rock phosphate particles was used as a P fertilizer by Guimarães *et al.* (2018). This composite, obtained *via* low-temperature extrusion, was encapsulated by the oxidizing microorganism *Aspergillus niger*. It was shown to be effective in increasing S^0 oxidation while improving P supply through PHR dissolution in an acidic medium.

The main disadvantage of S coating is the fragility of the film created on the surface of the fertilizer, which can crack easily (Zhang and Yang, 2021). Moreover, soil acidification can occur when using S as a coating agent (Zhao *et al.*, 2017; Ma *et al.*, 2020). It can also be easily destroyed by soil bacteria. In order to enhance the coating quality, expensive sealants and conditioners are required for the preparation of S coating-based fertilizer, which increases its manufacturing costs (Behin and Sadeghi, 2016).

Polymer-based SCRFs

Various polymers like chitosan, alginate, cellulose, and their derivatives have been used to control nutrient release due to their biodegradability, nontoxicity, and low cost (Ahmad *et al.*, 2015; Messa and Faez, 2020; Sim *et al.*, 2021). Compared to inorganic coatings, biodegradable polymers result in greater control of the active component release (Daitx *et al.*, 2019). Polymeric materials can be applied in various physical forms, including hydrogels, powders, solutions, and melts (Shavit *et al.*, 2003; Bortolin *et al.*, 2013; Daitx *et al.*, 2019).

Nutrient release rate can be affected by several factors, including the chemical and mechanical features of the materials, their biodegradability, and the properties of the release medium (Daitx *et al.*, 2019). A high degradation rate of the carrier system results in a fast release of the active components. Moreover, fragile materials tend to release nutrients at a faster rate. Daitx *et al.* (2019) studied a biodegradable polymer based on poly(hydroxybutyrate) to evaluate the relationship between the polymer feature and nutrient release kinetics. For this, two SCRFs were investigated: the first using NPK fertilizer directly incorporated within the polymeric matrix and the second consisting of the fertilizer incorporated in bentonite and blended with the polymer. All the systems showed a significant decrease in nutrient release compared to the direct application of NPK. A nutrient release rate of up to 37% was noted for the first SCRF over 240 h, while a greater control of the nutrient release behavior was noted for the second SCRF, with a release rate ranging from 4% to 11% for the same period. The interaction between bentonite and poly(hydroxybutyrate) led to a slow degradation of the polymer matrix, and consequently, the nutrient release kinetics became very slow throughout the experiment. Soybean protein isolate and poly(lactic acid) blends plasticized with triacetin were investigated as the matrix material for controlled-release fertilizers (Calabria *et al.*, 2012). The results showed good control in the release of NPK nutrients for about 5 d, and no significant changes were noted in the matrix structure or in the chemical structure and content of the NPK nutrients after injection molding, a method used to obtain molded products by injecting molten materials into a mold, suggesting that these fertilizers can undergo melt processing without any biodegradation. Messa and Faez (2020) investigated the effect of chitosan and nanocellulose combination on fertilizer delivery properties. The chitosan microparticles induced a decrease in the initial release rate of NPK, resulting in extended release of the entrapped nutrients (up to 2 h). The addition of nanocellulose (10% by weight) to the microparticles induced the most significant decrease in fertilizer release rate (within 5 h), and the release behavior of NPK-containing microparticles was governed by the electrostatic interaction between components and the barrier capacity of the coating solution.

Recently, bio-based coating materials have been introduced in order to design more eco-friendly SCRFs (Liang *et al.*, 2019). Natural polymers are frequently combined with synthetic polymers for SCRFs due to their short lifetime (less than 30 d), numerous microholes, and hydrophilic groups (Liang *et al.*, 2019). The slow-release property of a DAP fertilizer coated using sodium alginate and chitosan biopolymers was evaluated as a strategy to improve the use efficiency of DAP and reduce its loss in soils (Dhanalakshmi *et al.*, 2022). The study revealed that the use of both chitosan and alginate on DAP granules resulted in a slower initial release of DAP compared to granules coated with only one polymer. A chitosan-kaolinite coating material also resulted in good slow-release behavior for NPK fertilizers (Eddarai *et al.*, 2022). Fertahi *et al.* (2020) investigated the efficiencies of biopolymers based on three natural polysaccharides, *i.e.*, carboxymethyl cellulose (CMC), alginate, and kappa-carrageenan, as coating materials for TSP fertilizer.

Slow and controlled P release was obtained for the fertilizer coated with lignin-kappa-carrageenan composite for 3 d. In addition, about 59.5% and 72.5% of P were released after 3 d for the TSP/biopolymer ratios of 5:1 and 15:1, respectively. In contrast, a complete release (100%) of P was achieved for the uncoated TSP during the same period.

The effect of the number of chitosan-coating layers on the release rate of P was studied, and the results revealed that the release rate of P was higher with the single-coated granules than with triple-coated granules. Three different coated NPK fertilizers prepared using cellulose acetate, polyacrylonitrile, and polysulfone were investigated to evaluate the impact of the polymer coatings and their morphologies on the release of macroelements (Jarosiewicz and Tomaszewska, 2003). It was revealed that an increase in coating thickness or polymer content decreased the coating porosity, with the highest porosity found in cellulose acetate compared to polysulfone and polyacrylonitrile. Moreover, the investigation demonstrated that the nutrient release rate diminished when increasing the polymer content or the number of coating layers. The highest NPK release rate was noted for cellulose acetate-coated fertilizer (after 5 h) compared to the polyacrylonitrile- and polysulfone-coated fertilizers. The low release rates of NPK from the polyacrylonitrile- and polysulfone-coated fertilizers were assigned to their high hydrophobicity as well as their low porosity.

Superabsorbent hydrogel-based SCRFs

Superabsorbent hydrogels or superabsorbents are tridimensional structures created through a crosslinked hydrophilic polymer. They are defined as hydrophilic polymers with high absorption capacity for water or aqueous solutions (Klinpituksa and Kosaiyakanon, 2017; Rather *et al*., 2022). It can be applied as a carrier matrix or coating material. Hydrogel-based fertilizers can be made using synthetic hydrogels, natural hydrogels, or a combination of both. Synthetic hydrogel-based fertilizers are generally prepared with acrylamide and acrylic acid (AAc). However, due to the weak thermal and mechanical features, poor biodegradability, and high production cost of petroleum-based hydrogel, a combination of synthetic polymer and natural components has often been used to prepare hydrogel-based SCRFs with improved release kinetics, swelling ratio, biodegradability, and mechanical and thermal properties (Alharbi *et al*., 2018; Al Rohily *et al*., 2020; Kenawy *et al*., 2020).

The controlled-release property of superabsorbent phosphate-bound alginate-graft-polyacrylamide was investigated by Al Rohily *et al*. (2020) at normal pH and 25 °C. In this study, monoammonium phosphate (MAP) and DAP fertilizers reacted with alginate and poly(vinyl alcohol). Then, the phosphorylated matrix was grafted with acrylamide. A P release rate of up to 77% was noted for the MAP sample and about 57% for the DAP sample during 45 d of the application. Moreover, the developed fertilizers were able to release P efficiently, with a slight decrease observed in a calcium chloride ($CaCl_2$) medium, suggesting that the presence of the polymer alginate in the fertilizer structure may extend the availability of P over time for the plant. A controlled-release fertilizer hydrogel based on phosphate-bound carboxymethyl starch-graft-polyacrylamide was developed by Alharbi *et al*. (2018) to deliver the phosphate fertilizer to the plant at a constant rate. In this study, two types of starch phosphate monoesters were synthesized using MAP and DAP. The results revealed that both samples showed a similar cumulative P release rate of about 87% during the 30 d of the experiment. Analysis of release data indicated that the P release process from the examined fertilizers followed a quasi-Fickian diffusion mechanism. The release behavior of P in superabsorbent hydrogels based on polyacrylamide/cashew tree gum was investigated (Sousa *et al*., 2021). The results revealed a fast increase in the concentration of fertilizer released at the first stage, and then a sustained release was achieved after 4 h. The rapid initial release of the nutrient was attributed to the dissolution of the fertilizer particles adsorbed on the surface. The mathematical analysis of the release data by the Korsmeyer-Peppas model showed that the nutrient elution process occurred through a diffusion process.

Baki and Abedi-Koupai (2018) reported a similar behavior for a superabsorbent slow-release fertilizer consisting of polyacrylamide grafted with alginate and biochar. Polymer based on sulfonated corn starch/polyAAc embedding PHR (SCS/PAA/PHR) was investigated by Zhong *et al*. (2013). The results proved that the developed SCS/PAA/PHR system exhibited good sustained and controlled-nutrient-release capacity, and that SCS/PAA could improve P release greatly. After 30 d, the P release ratio from SCS/PAA/PHR was raised by about 40% and 350% compared to corn starch/polyAAc/PHR (CS/PAA/PHR) and PHR, respectively. This was explained by the dissolution of some of the insoluble PHR by the acidic microenvironment in the swollen hydrogel. It was demonstrated that the amount of NPK released was reduced by adding montmorillonite (MMT) into alginate-*g*-poly(AAc-*co*-acrylamide)/NPK hydrogel, compared to the pristine alginate-*g*-poly(AAc-*co*-acrylamide)/NPK hydrogel (Rashidzadeh and Olad, 2014). This behavior was due to the formation of a tortuous path caused by the presence of the sodium MMT within the hydrogel matrix. Polymer-based polysaccharides are commonly used to produce pure natural hydrogel-based fertilizer (Klein and Poverenov, 2020). The NPK release rate was studied at room temperature in distilled water from polyAAc-based hydrogel fertilizer (Teodorescu *et al*., 2009). The results demonstrated that the NPK release rate was affected by the ratio of the crosslinking agent N,N'-methylenebisacrylamide (MBA) to the matrix-forming component AAc. A slow dissolution process was achieved at a high ratio of MBA/AAc due to the high content of crosslinking agent, which leads to a compact fertilizer structure.

Despite these findings, the long- and short-term effects of certain superabsorbents on soil health remain insufficiently studied. While they can enhance soil agglomeration and water retention, their impact on soil components (such as the microbiome) requires further investigation (Wilske *et al.*, 2014).

NANOFERTILIZERS

Nanofertilizers are defined as fertilizers with a single unit between 1 and 100 nm in size in at least one dimension (Liu and Lal, 2015). These nanofertilizers exist in three categories: i) nanoscale fertilizer, shrunk in size in the form of nanoparticle, ii) fertilizer with nanoadditive, and iii) fertilizer with nanocoating (Mastronardi *et al.*, 2015) (Fig. 2). Nanofertilizers are either nanomaterials that can supply one or several nutrients to crops and improve their growth and productivity, or fertilizers that use nanoscale materials that do not directly provide nutrients to plants but rather enhance the efficiency of CFs. Furthermore, nanofertilizers could be classified as macronutrient and micronutrient nanofertilizers, hybrid nanofertilizers, organic nanofertilizers, and carbon-based nanofertilizers (Arora *et al.*, 2024). These nanofertilizers are expected to enhance plant growth and yield, improve fertilizer use efficiency, and avoid nutrient loss compared to CFs.

Macronutrient nanofertilizers

The low use efficiency (15%–20%) of traditional P-fertilizers is a serious issue in agriculture. This problem may be overcome *via* the encapsulation of phosphates in a nanocarrier structure (Subramanian and Thirunavukkarasu, 2017). It was reported that dihydrogen phosphate ($H_2PO_4^-$) ions can be released from a mineral mixture of PHR (primarily apatite) and zeolite and used by plants (Eberl, 2008). For maize plants (grown for 30 d) treated with various phosphate nanoparticles, the highest shoot length, root length, biomass, absorbed P amount, and dry matter were noted in the HA (200 nm) treatment, resulting from CaP (100 nm) and nano-PHR (42 nm). Liu and Lal (2014) prepared HA nanoparticles (16 nm) and evaluated the fertilizing effect on soybean using an inert culture medium in a greenhouse experiment. The results revealed that the use of these nanoparticles improved the growth rate by about 33% and the seed yield by 20% as compared to TSP. Moreover, the aboveground and belowground biomasses increased by 18% and 41%, respectively. The HA nanoparticles are also able to supply plants with calcium (Ca) in addition to P. The effects of two types of PHR nanoparticles (34% and 31% of phosphorus pentoxide (P_2O_5)) and simple superphosphate on the growth of maize were evaluated under field conditions (Adhikari *et al.*, 2014). The results revealed that the grain and stover yields were much higher in the nanoscale Udaipur PHR (34% P_2O_5) treatment as compared to the control. It was also revealed that the P effectiveness was the same in the forms of PHR particles and simple superphosphate. Despite the yield being slightly lower in the form of PHR particles compared to simple superphosphate, the PHR can be used as a non-expensive source because only the grinding process was used for its preparation. Nanoscale P fertilizer enhances the P use efficiency and diminishes the different forms of P losses.

Calcium is a crucial element for cell wall stabilization, seed development, and the neutralization of hazardous chemicals. A small amount of Ca nanofertilizer raised pomegranate quality and yield in comparison with the $CaCl_2$ treatment (Davarpanah *et al.*, 2018). Similarly, Ranjbar *et al.* (2020) reported that spraying Ca nanofertilizer on apple fruit during the preharvest period enhanced the qualitative and quantitative features over $CaCl_2$. Spray of Ca nanofertilizer (500 mg L^{-1}) led to 56.3% higher flowering in addition to the 15-d flowering advancement as compared to the control (Seydmohammadi *et al.*, 2020). Calcium carbonate ($CaCO_3$) and calcium nitrate ($Ca(NO_3)_2$) nanofertilizers were tested on groundnut by Liu *et al.* (2005), who demonstrated that the application of these Ca nanofertilizers resulted in an increase in groundnut. The use of $CaCO_3$ nanoparticles (160 mg L^{-1} Ca) as a Ca nutrient significantly enhanced peanut seedling growth, Ca retention, and root-to-shoot transport compared to the control (without Ca). Improvement in dry biomass was noted in seedlings treated with soluble $Ca(NO_3)_2$ (200 mg L^{-1}). It was reported that the plant roots can absorb and transport the Ca nanoparticles from roots to shoots, as the Ca

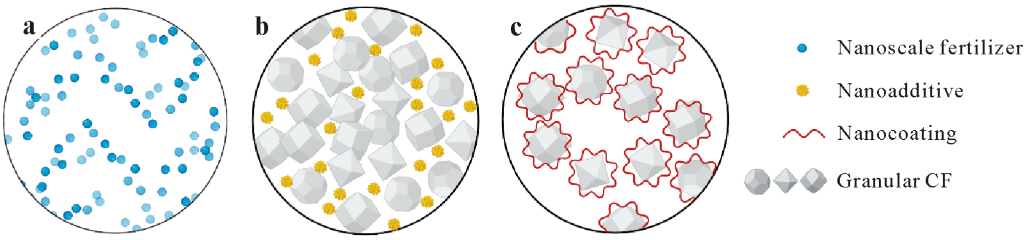

Fig. 2 Schematic diagrams showing three categories of nanofertilizers: nanoscale fertilizer (a), fertilizer with nanoadditive (b), and fertilizer with nanocoating (c). CF = conventional fertilizer.

contents in seedling stems (30.4 g kg^{-1}) and roots (15.8 g kg^{-1}) were higher after the application of Ca nanoparticles compared to the control (5.8 g kg^{-1} in seedling stem and 4.3 g kg^{-1} in roots).

Micronutrient nanofertilizers

Plant micronutrients include copper (Cu), zinc (Zn), manganese (Mn), iron, and molybdenum, among others. In comparison with macronutrients, only trace amounts of micronutrients are needed to increase crop growth and food production (Liu and Lal, 2014). Micronutrients are often combined at low concentrations (< 5 mg L^{-1}) with N, P, and K fertilizers as soluble salts for plant uptake. Micronutrient fertilizers in the composite form usually provide an appropriate amount of nutrients. Nevertheless, the availability of micronutrients applied to plants may be limited, and micronutrient deficiency may arise in some coarse-textured soils with low organic matter or soils with an alkaline pH. Micronutrients delivered in the form of nanofertilizers can improve their availability to plants. Since the development, as well as the use of nanofertilizers, is in the initial stages, few studies have investigated the influence and advantages of using micronutrient nanofertilizers. Liu and Lal (2014) summarized most studies on micronutrient-containing nanoparticles.

HA AND HA-BASED FERTILIZERS

HA and its ion-exchange property

As one of the main components of animal and human bone tissues, HA has been largely used in the biomedical field as a bone fracture repair and as a drug delivery system owing to its bioactivity and biocompatibility (Mondal and Pal, 2019; Ait Said *et al.*, 2021, 2023a, b; Sajadinia *et al.*, 2021). In agriculture, HA nanoparticles have been considered as an effective nanomaterial for plant P nutrition (Kottegoda *et al.*, 2017; Maghsoodi *et al.*, 2020). Other reasons are their high reactivity, stability, their use as a source of Ca nutrition besides P nutrition, and their ability to alleviate heavy metal stress in plants.

Hydroxyapatite nanoparticles can leverage their fertilizing potency in two forms: as SCRFs or as nanocarriers for the release of macro- or micronutrients. In the first case, the mode of action is based on the dissolution of HA nanoparticles in water, since they are less soluble in aqueous solutions compared to commercial fertilizers, providing a delayed and more controlled release of P. In the second scenario, HA nanoparticles reach plant tissues, where they either exert their effect while preserving their structure or dissolve to deliver P and other nutrients (Yoon *et al.*, 2020).

The doping of HA particles with cations and anions has attracted a great deal of attention in recent decades. The HA properties at the nanoscale, when combined with synergistic effects induced by the doping of different ions or the incorporation of various molecules, would be beneficial for the design of advanced nanofertilizers with slow/controlled-release properties (Megalathan *et al.*, 2016; Abeywardana *et al.*, 2021). It was reported that HA nanoparticles can be used as an efficient adsorbent to treat cadmium (Cd)-contaminated soils (Li and Huang, 2014), leading to decreased plant uptake and improved resistance to Cd-induced stress.

The chemical substitution in HA can take place either at cationic or anionic sites. The added species can affect the physicochemical features of the material, improving its reactivity and performance without affecting its structure. In the cationic sites, the Ca ions can be substituted by the ions of transition metals (*e.g.*, cobalt, nickel, Mn, Cu, Zn, and Cd), alkaline earth metals (*e.g.*, barium, strontium, and Mg), or other metals (*e.g.*, aluminum, lanthanum, and lead). Anionic substitutions involve either phosphate (PO_4^{3-}) or hydroxyl (OH^-) ions, or both. The PO_4^{3-} ions can be substituted by hydrogen phosphate (HPO_4^{2-}), arsenate (AsO_4^{3-}), vanadate (VO_4^{3-}), sulfate (SO_4^{2-}), silicate (SiO_4^{4-}), or carbonate (CO_3^{2-}) ions, while OH^- can be substituted by fluoride (F^-), chloride (Cl^-), bromide (Br^-), oxide (O^{2-}), or CO_3^{2-}. For carbonated apatite, the substitution with carbonate species can be performed at two sites as indicated in the formula: $Ca_{10-x}(PO_4)_{6-x}(CO_3)_x(OH)_{2-2y}(CO_3)_y$ (Dorozhkin, 2015; Ait Said *et al.*, 2023a). The replacement of phosphate and hydroxyl ions by carbonate can lead to A- and B-type carbonated apatite, respectively.

HA-based fertilizers

Studies reporting the effects of HA-based fertilizers on plant growth are presented in Table I. The effect of HA nanoparticles, obtained by ultrasound and microwave methods, on both the morphological and physiological features of maize plants was investigated (Sajadinia *et al.*, 2021). The results revealed that the use of HA nanoparticles as P fertilizers can enhance the physiological and growth features of maize compared to simple superphosphate and TSP fertilizers. The influences of HA nanoparticles on the biomass, antioxidant enzyme activities, contents of chlorophyll, malondialdehyde, and vitamin C, and Cd uptake of pak choi in Cd-contaminated soil (10 mg kg^{-1}) were studied through a pot experiment (Li and Huang, 2014). Results revealed that the biomass of plant increased by 8.0%, 13.2%, 19.5%, and 20.2% using 5, 10, 20, and 30 g kg^{-1} HA, respectively. Shoot Cd decreased by 27.1%, 44.2%, 50.9%, and 62.4%, respectively. The authors showed that the supplement of the HA particles improved the contents of vitamin C and chlorophyll and reduced the malondialdehyde level in plant shoots. Moreover, increases in superoxide dismutase, catalase, and peroxidase activities were observed. The findings confirmed that the use of HA as a fertilizer could reduce plant retention of heavy metals like Cd in contaminated soils.

TABLE I

Effects of hydroxyapatite (HA)-based fertilizers on plant growth

Fertilizer[a)]	Plant(s)	Effects(s)[b)]	Reference
HA	Cress, corn	Improved cress seed germination, stimulated corn coleoptile development	Carella *et al.*, 2021
HA nanoparticles (nHA)	Radish	Improved shoot and root elongation and dry biomass	Madanayake *et al.*, 2021
	Maize	Enhanced plant growth and physiological characteristics	Sajadinia *et al.*, 2021
	Pak choi	Increased leaf chlorophyll and vitamin C contents, reduced leaf malondialdehyde content in plant shoots, increased SOD, POD, and CAT activities	Li and Huang, 2014
	Rosemary	Improved plant productivity	Elsayed *et al.*, 2022
	Tomato	Significantly stimulated root elongation	Marchiol *et al.*, 2019
	Sunflower	Improved shoot and root fresh biomasses	Xiong *et al.*, 2018a
	Chickpea	Enhanced germination and plant growth	Bala *et al.*, 2014
Urea-HA	Maize	Improved dry matter production	Giroto *et al.*, 2024
Urea-HA-MMT	Rice	Significantly improved crop yield	Madusanka *et al.*, 2017
Zn-doped urea-HA	Maize	Significantly improved germination rate and plant growth and development	Abeywardana *et al.*, 2021
Fe-modified HA/polydopamine/amino C nanotube	Coriander	Promoted plant growth	Tang *et al.*, 2024
Cellulose-graft-poly(acrylamide)/nHA	Maize	Improved plant dry matter and yield	Rop *et al.*, 2019
CMC-stabilized nHA	Soybean	Enhanced plant growth and yield	Liu and Lal, 2014

[a)] MMT = montmorillonite; CMC = carboxymethyl cellulose.

[b)] SOD = superoxide dismutase; POD = peroxidase; CAT = catalase.

The phytotoxicity of HA extracted from fishery byproducts (fish bones) *via* thermal conversion was assayed against cress seed, and its biostimulation activity was tested on corn seedlings and coleoptiles (Carella, 2021). Good results were obtained in terms of cress, seedling germination and corn coleoptile biostimulation. Abeywardana *et al.* (2021) developed a new nanoseed coating based on Zn-doped urea-HA through a one-pot *in situ* sol-gel approach. The developed nanoseed coating significantly increased the seed germination rate and seedling growth of maize by *ca.* 19% and 69%, respectively. Nanoscale HA was developed as a P nanofertilizer to enhance the production of rosemary plants (Elsayed *et al.*, 2022). The results indicated that the use of 0.5 and 1 g L^{-1} HA nanoparticles improved the growth and essential oil production as compared to the conventional form. Moreover, the highest values of stem-related parameters (pith diameter, overall stem diameter, and thickness of the phloem, fiber, and xylem tissues) as well as leaf-related parameters (midvein thickness and lamina thickness) were obtained using HA nanoparticles, demonstrating their potential for improving the production of rosemary plants.

In addition to serving as a source of P, HA nanoparticles have also been proposed as an N fertilizer when combined with urea, which can provide improved fertilization efficiency and reduce the associated adverse environmental effects (Xiong *et al.*, 2018a; Maghsoodi *et al.*, 2020). A recent study by Maghsoodi *et al.* (2020) investigated the efficiency of HA as a slow-release N fertilizer in both simple water and a calcareous waterlogged soil. The results showed a controlled release of N due to the interaction between the urea molecules and HA nanorods. The urea-HA reduced urea release by 11.5 times as compared to the urea alone. Moreover, the release kinetics of urea from the HA matrix were fitted by the Korsmeyer-Peppas model, suggesting a Fickian diffusion process. Kottegoda *et al.* (2017) observed a significantly slower release of N from urea-HA nanoparticles when compared to conventional urea. In another study, the effects of urea-HA and conventional urea on both seed germination and seedling growth of mung bean were compared. The nanohybrid provided better results of both germination and biomass yield compared to the traditional urea (Subbaiya *et al.*, 2012). The N agronomic use efficiency in rice plants supplied with urea-HA was evaluated (Kottegoda *et al.*, 2017). The slower N release from urea-HA led to better N efficiency as compared to the conventional urea fertilizer.

Several factors influence the performance of HA-based nanofertilizers in soil. For example, HA nanoparticles with different hydrodynamic sizes and surface charges were prepared *via* co-precipitation, and their efficiencies as P fertilizers were evaluated in P-deficient Ultisol and Vertisol (Xiong *et al.*, 2018b). The HA nanoparticles exhibited a better controlled-release profile for P in the acidic Ultisol compared to TSP, which was very soluble. However, the developed HA compounds had no significant effect on P availability in the Vertisol (pH *ca.* 8.2) due to their low solubility in this alkaline soil. The authors also evaluated the effect of the surface charge of HA nanoparticles on P availability. The results indicated that the negative surface charge of HA nanoparticles might have certain advantages due to the fact that the HA nanoparticles can compete with phosphate ions for adsorption sites in the soil, thus resulting in more free phosphate ions in the soil environment. In another study, Xiong *et al.* (2018a) investigated the benefit of HA nanoparticles of different surface charges as fertilizers using sunflowers in two types of P-deficient soils (Ultisol and Vertisol). In the acidic Ultisol (pH *ca.* 4.7), HA nanoparticles with a surface charge of -13.8 mV were more effective in delivering P than those with surface charge values of 22.1 and -1.37 mV. However, all the HA compounds did not improve plant growth in the Vertisol (pH *ca.* 8.2). The efficiency of nanoscale HA particles (20 nm) in P-adsorbing Andisols and Oxisols compared to bulk HA (600 nm) was evaluated by Montalvo *et al.* (2015). The results revealed greater mobility of HA nanoparticles in Andisols than in Oxisols. For bulk HA, no P was detected in the leachates from both soils due to the large HA particle size. The plant uptake of P that was derived from the fertilizers examined in the two soils was in the order: TSP $>$ HA nanoparticles $>$ bulk HA. These investigations indicate the need for further studies to evaluate the suitability of HA nanoparticles because they are affected by soil features. It is also interesting to know how HA modification influences its mobility and reactivity in soils. For example, surface charge modification of HA nanoparticles would significantly alter how they react with charged soil particles.

Although some negative effects of HA on plants have been demonstrated, these are often assigned to the structure of HA and the high content of Ca^{2+} in cells. Many studies have tested the cytotoxicity of HA particles in cancer cells (Wang *et al.*, 2012; Jiang *et al.*, 2014), but very few researchers have investigated the interaction mechanism between HA and plant cells. Jiang *et al.* (2014) used plant cells to evaluate the link between the biocompatibility and cytotoxicity of HA. The cytotoxicity of HA nanoparticles was evaluated on mung bean sprouts by measuring their hypocotyl length. The results revealed that the presence of HA nanoparticles inhibited the growth of mung bean sprouts, and the hypocotyl length of mung bean sprouts cultured in a medium containing HA nanoparticles (5 mg mL^{-1}) was the shortest. The authors reported that the nanostructure character and Ca content were considered as the main parameters to cause cell apoptosis, resulting in the inhibition of the growth of mung bean sprouts. The effects of HA nanoparticles on the Cd-induced root growth inhibition of various plants (tomato, carrot, cucumber, and lettuce) were investigated in the short term compared to kaolin, MMT, magnetite, hematite, and maghemite (Wang *et al.*, 2012). Root growth of all examined plants was not inhibited in the presence of nanoparticles, except for HA on tomatoes. Different possibilities for the HA-induced cell death have been considered: i) high local concentration of intracellular Ca^{2+}, ii) the crystalline character of the HA nanoparticles, and iii) the adsorption of positively charged species onto the surface of HA nanoparticles (Shen *et al.*, 2002). Besides, HA nanoparticles can interact with some organic molecules to generate free radicals of high energy level. It was proven that the negatively charged radicals remain and create reactive oxygen species (ROS) that can induce cell death by disrupting the regulation of Ca^{2+} carriers or through destroying protein, fat, and DNA (Maghsoodi *et al.*, 2020). The formation of ROS by HA has been evidenced, which can lead to the lipid peroxidation in cell membrane, disturb biochemical and physiological processes, damage biological molecules, and cause plant death (Khan *et al.*, 2017). Albrecht *et al.* (2009) studied the effects of various HA compounds on rat alveolar NR8383 cells and primary macrophages and showed that the cytotoxicity was raised with the production of ROS. Intracellular Ca species have been demonstrated to be the main contributors to cell death (Burek *et al.*, 2003; Shilo *et al.*, 2003; Maghsoodi *et al.*, 2020). The local content of intracellular Ca^{2+} was significantly increased, beyond the typically absorbed amount, in mung bean sprout cells. It has been shown that Ca^{2+} ions can fragment DNA chains and activate endonuclease enzymes. These ions also promote the activation of phosphatase calcineurin, which participates in the Bcl2-associated death promoter dephosphorylation, which enhances heterodimerization and subsequently leads to cell death (Wang *et al.*, 1999).

It is very likely that the solubility and other properties (reactivity, uptake, and release ability) of HA will be enhanced when HA is combined with organic macromolecules like natural and synthetic polymers. Furthermore, the reactivity of the HA active sites enables the functionalization of its surface for the preparation of multifunctional nanocomposites.

HA composite-based fertilizers

Studies exploring the mobility of HA and phosphate ions through the soil profile concluded that their application under alkaline soil (pH *ca.* 10.5) facilitated their movement through pores and avoided the agglomeration of particles. Yet, HA was found to be highly insoluble under such environments. However, at pH *ca.* 6.5, 10% of the substance was dissolved and thus ready for root uptake, although the nanoparticles agglomerated (Wang *et al.*, 2015). A reasonable way to address these difficulties and increase HA nanoparticle availability is to tweak their surface chemistry with safe and soil-friendly compounds that may promote HA solubility while preventing nanoparticle agglomeration (Yoon *et al.*, 2020).

Currently, intensive research studies are directed toward formulating inorganic-organic composites for SCRFs. Nanoparticles of HA can be incorporated into a polymer-based hydrogel matrix to create a composite for slow and controlled release of P. Besides being physically fixed within the copolymer, the hydroxyl (–OH) functional groups of HA nanoparticles can interact with the monomer, making it part of the network. Rop *et al.* (2020) attempted to produce a polymer nano-composite fertilizer by grafting cellulose with AAc in the presence of HA nanoparticles. The formulated composite was suggested as a potential candidate for agricultural use as a slow-release fertilizer and soil conditioner, especially in arid/semi-arid areas. The incubation tests demonstrated low mineral N content over the first 4 weeks and a peak during the 12th week related to the most nutrient-demanding stages of development and reproduction of most crops. The authors reported that the raised P availability after more than 4 weeks in all formulations could be explained by P release *via* microbial solubilization of HA nanoparticles and the degradation of the polymeric phase. Liu and Lal (2014) investigated CMC-stabilized HA nonfertilizer suspension and observed higher mobility of nanofertilizer in soil when compared to HA nanoparticles without CMC, indicating a better P supply to the root system. Moreover, the results revealed enhanced growth (by 32.6%) and yield (by 20.4%) of soybean compared to the calcium dihydrogen phosphate treatment. Rop *et al.* (2019) studied the responses of maize, capsicum, and kale to a cellulose-graft-poly(acrylamide)/HA nanoparticles slow-release NPK fertilizer to identify its agronomic optimal use rates in a Nitisol soil group in Kabete, Kiambu County, Kenya. The performance parameters were not significantly different between the slow-release fertilizers and CFs at the same rate. The developed slow-release fertilizer showed improved capsicum fruit numbers and dry matter yield, maize grain yield, and kale dry matter yield. Nitrogen deficiency was noted for CF-treated maize at the 8th week, but not for maize treated with SCRF at similar or higher rates. This was attributed to the synchrony of N release from the investigated SCRF with crop requirement. The agronomic optimal application rates of SCRFs were higher than CFs, suggesting improved NUE even at higher SCRF doses. The developed SCRFs can, therefore, be an alternative to CFs as they are eco-friendly and easy to synchronize, thus providing improved NUE and environmental protection. In another study, Rop *et al.* (2018) investigated the potential of cellulose-graft-poly(acrylamide)/HA nanoparticles/soluble fertilizer nanocomposite to improve NUE. Significantly, lower mineral N content was noted during the first four weeks in SCRF treatments compared to CF and the control. Moreover, the study revealed that a significantly higher P amount was measured in the 4th week for CF in comparison to the SCRF, whereas some of the examined SCRFs released significantly higher P content than CF during the 8th week. The synergistic effects of polymer-coated urea-HA and lignin on urea release rate were evaluated (Elhassani *et al.*, 2019). The results showed that urea-HA encapsulated using lignin appeared to be a versatile and efficient slow-release fertilizer. Based on the obtained results, the urea release profile of the urea-HA encapsulated by lignocellulosic biomass-extruded composite fertilizer decreased significantly (60 d of release) compared to that of native urea in which the dissolution process occurred rapidly (< 1 d) due to the saturation of the solution around urea. In this case, the presence of HA causes the fertilizer to release urea in a slower manner due to the strong interfacial interactions between the N–H group of urea and the HA active sites.

Some other studies focused on highly complex structure-based nanofertilizers involving HA nanoparticles. Particularly, the fertilizing abilities of urea-HA-MMT and urea-HA encapsulated into wood chips were evaluated on *Festuca arundinacea*. It was shown that both composites reduced N leaching and induced a slower N elution when compared to traditional fertilizers (Gunaratne *et al.*, 2016). More recently, Madusanka *et al.* (2017) conducted a life cycle test on rice using urea-HA-MMT. A significant diminution in N release rate from soil columns and improvement of crop yield were recorded. The effects of HA particles stabilized with CMC were analyzed on the germination process, seedling growth, and metabolism of tomato (Marchiol *et al.*, 2019). The study proved that the germination rate of tomato was not affected by HA content, whereas root elongation was significantly stimulated. This indicates that the HA nanoparticles had no phytotoxic effect on tomato and could be used as a P carrier. Nevertheless, the use of SCRFs is still hindered, especially in developing countries, due to the higher production cost compared to most CFs. Thus, it is crucial to develop new and efficient technologies to produce low-cost fertilizers through effective and targeted delivery. Amounts supplied to the plant should be adequate and efficient to improve yields and returns without causing any environmental impact. This can be achieved by optimizing fertilizer application rate, as defined in both agronomic and economic perspectives. From the agronomic point of view, this is the rate of fertilizer application over which a further addition has no effect on crop yield, and, from an economic point of view, it is the minimum rate of fertilizer necessary to maximize profits. In most cases, the impact of fertilizers on plant yield can be assessed using fertilizer response functions, which are fitted to fertilizer rate trial data *via* regression analysis for the purpose of forecasting. Curve fitting approaches have been explored to estimate optimal fertilizer application rates.

CONCLUSIONS AND FUTURE PERSPECTIVES

Excessive use of CFs is primarily driven by their low NUE, which leads to reduced crop yields and increased fertilization costs. Additionally, this practice has detrimental environmental consequences, including air and water pollution caused by nutrient volatilization, leaching, and surface runoff. To address this issue, the utilization of novel SCRFs in agriculture has emerged as a promising trend. Extensive research has focused on the development of different SCRFs using polymer-, hydrogel-, inorganic-, and composite-based formulations to overcome these challenges. Recently, CaP compounds such as HA-based fertilizers have been attracting more interest due to their high reactivity and adsorption capacity. However, the use of HA-based fertilizer is still limited due to its weak solubility. Moreover, some studies suggest that the use of HA nanoparticles has a negative impact on plant growth and causes cell death. The development of HA-polymer composite-based fertilizers has been proposed as a novel strategy to enhance the properties of HA-based fertilizers like solubility, reactivity, and release ability. Nevertheless, the release process of HA nanocomposite-based fertilizer depends on the composition of the encapsulating/coating substrate. The evaluation of the nutrient interaction mechanisms might provide a theoretical basis for controlling HA-based and HA-polymer-based fertilizers, as the features and efficiency of the fertilizers are strongly dependent on the nature of the precursors and the preparation conditions. While synthetic polymers used as organic phases offer certain advantages, their reliance on organic solvents poses risks to ecosystems. Additionally, these polymers accumulate in soil once nutrients are depleted, potentially leading to the accumulation of undesirable plastic residues. To address these concerns, the development of eco-friendly nanocomposites utilizing biopolymers sourced from agro-industrial wastes and biomass presents a viable alternative. Few studies have been conducted on the nutrient release mechanisms and economic assessment of HA and its composite-based fertilizers. Besides, the effects of parameters such as polymeric content and inorganic/organic ratio on soil features, nutrient release, and plant growth under different conditions remain unclear.

Since there is still a lack of fundamental understanding regarding the positive and negative impacts of HA-polymer-based SCRFs, it is essential to conduct a comprehensive investigation to further explore the potential of these precision fertilizers. The development of controlled-release nanofertilizers with specific particle sizes and controlled-nutrient-release processes holds promise for optimizing nutrient release rates and enhancing nutrient uptake efficiency. This approach ensures appropriate nutrient absorption by crop plants, minimizes toxicity, and reduces environmental pollution compared to CFs. However, it is worth noting that despite the potential benefits of controlled-release nanofertilizers in promoting sustainable agricultural practices and improving yields for healthier agricultural production, the cost-effectiveness of related technologies remains a challenge.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES

Abeywardana L, de Silva M, Sandaruwan C, Dahanayake D, Priyadarshana G, Chathurika S, Karunaratne V, Kottegoda N. 2021. Zinc-doped hydroxyapatite-urea nanoseed coating as an efficient macro-micro plant nutrient delivery agent. *ACS Agric Sci Technol*. **1**: 230–239.

Adhikari T, Kundu S, Meena V, Rao A S. 2014. Utilization of nano rock phosphate by maize (*Zea mays* L.) crop in a Vertisol of Central India. *J Agric Sci Technol*. **4**: 384–394.

Ahmad N N R, Fernando W J N, Uzir M H. 2015. Parametric evaluation using mechanistic model for release rate of phosphate ions from chitosan-coated phosphorus fertiliser pellets. *Biosyst Eng*. **129**: 78–86.

Ait Said H, Mabroum H, Lahcini M, Oudadesse H, Barroug A, Ben Youcef H, Noukrati H. 2023a. Manufacturing methods, properties, and potential applications in bone tissue regeneration of hydroxyapatite-chitosan biocomposites: A review. *Int J Biol Macromol*. **243**: 125150.

Ait Said H, Noukrati H, Ben Youcef H, Mahdi I, Oudadesse H, Barroug A. 2023b. *In situ* precipitated hydroxyapatite-chitosan composite loaded with ciprofloxacin: Formulation, mechanical, *in vitro* antibiotic uptake, release, and antibacterial properties. *Mater Chem Phys*. **294**: 127008.

Ait Said H, Noukrati H, Oudadesse H, Ben Youcef H, Lefeuvre B, Hakkou R, Lahcini M, Barroug A. 2021. Formulation and characterization of hydroxyapatite-based composite with enhanced compressive strength and controlled antibiotic release. *J Biomed Mater Res A*. **109**: 1942–1954.

Al Rohily K, El-Hamshary H, Ghoneim A, Modaihsh A. 2020. Controlled release of phosphorus from superabsorbent phosphate-bound alginate-graft-polyacrylamide: Resistance to soil cations and release mechanism. *ACS Omega*. **51**: 32919–32929.

Albrecht C, Scherbart A M, Berlo D V, Braunbarth C M, Schins R P F, Scheel J. 2009. Evaluation of cytotoxic effects and oxidative stress with hydroxyapatite dispersions of different physicochemical properties in rat NR8383 cells and primary macrophages. *Toxicol Vitro*. **23**: 520–530.

Alharbi K, Ghoneim A, Ebid A, El-Hamshary H, El-Newehy M H. 2018. Controlled release of phosphorous fertilizer bound to carboxymethyl starch-*g*-polyacrylamide and maintaining a hydration level for the plant. *Int J Biol Macromol*. **116**: 224–231.

Arora P K, Tripathi S, Omar R A, Chauhan P, Sinhal V K, Singh A, Srivastava A, Garg S K, Singh V P. 2024. Next-generation fertilizers: The impact of bionanofertilizers on sustainable agriculture. *Microb Cell Fact*. **23**: 254.

Atalay S, Sargin I, Arslan G. 2022. Slow-release mineral fertilizer system with chitosan and oleic acid-coated struvite-K derived from pumpkin pulp. *Cellulose*. **29**: 2513–2523.

Baki M, Abedi-Koupai J. 2018. Preparation and characterization of a superabsorbent slow-release fertilizer with sodium alginate and biochar. *J Appl Polym Sci*. **135**: 45966.

Bala N, Dey A, Das S, Basu R, Nandy P. 2014. Effect of Hydroxyapatite nanorod on chickpea (*Cicer arietinum*) plant growth and its possible use as nano-fertilizer. *Iran J Plant Physiol*. **4**: 1061–1069.

Behin J, Sadeghi N. 2016. Utilization of waste lignin to prepare controlled-slow release urea. *Int J Recycl Org Waste Agric*. **5**: 289–299.

Bi S W, Barinelli V, Sobkowicz M J. 2020. Degradable controlled release fertilizer composite prepared *via* extrusion: Fabrication, characterization, and release mechanisms. *Polymers*. **12**: 301.

Bley H, Gianello C, da Silva Santos L, Priscila L, Selau R. 2017. Nutrient release, plant nutrition, and potassium leaching from polymer-coated fertilizer. *Rev Bras Ciênc Solo*. **41**: e0160142.

Bortolin A, Aouada F A, Mattoso L H C, Ribeiro C. 2013. Nanocomposite PAAm/methyl cellulose/montmorillonite hydrogel: Evidence of synergistic effects for the slow release of fertilizers. *J Agric Food Chem*. **61**: 7431–7439.

Burek C J, Burek M, Roth J, Los M. 2003. Calcium induces apoptosis and necrosis in hematopoetic malignant cells: Evidence for caspase-8 dependent and FADD-autonomous pathway. *Gene Ther Mol Biol*. **7**: 173–179.

Calabria L, Vieceli N, Bianchi O, de Oliveira R V B, do Nascimento Filho I, Schmidt V. 2012. Soy protein isolate/poly(lactic acid) injection-molded biodegradable blends for slow release of fertilizers. *Ind Crops Prod*. **36**: 41–46.

Carella F, Seck M, Esposti L D, Diadiou H, Maienza A, Baronti S, Vignaroli P, Vaccari P F, Iafisco M, Adamiano A. 2021. Thermal conversion of fish bones into fertilizers and biostimulants for plant growth—A low tech valorization process for the development of circular economy in least developed countries. *J Environ Chem Eng*. **9**: 104815.

Chen J, Lü S Y, Zhang Z, Zhao X X, Li X M, Ning P, Liu M Z. 2018. Environmentally friendly fertilizers: A review of materials used and their effects on the environment. *Sci Total Environ*. **613-614**: 829–839.

Daitx T S, Giovanela M, Carli L N, Mauler R S. 2019. Biodegradable polymer/clay systems for highly controlled release of NPK fertilizer. *Polym Adv Technol*. **30**: 631–639.

Davarpanah S, Tehranifar A, Abadía J, Val J, Davarynejad G, Aran M, Khorassani R. 2018. Foliar calcium fertilization reduces fruit cracking in pomegranate (*Punica granatum* cv. Ardestani). *Sci Hortic*. **230**: 86–91.

Dhanalakshmi M, Meena S, Ponnusamy J, Karthikeyan S, Nalina L. 2022. Effect of addition of biopolymer coated DAP on phosphorus release kinetics over an incubation time. *Res Crops*. **23**: 781–786.

Dorozhkin S V. 2015. Calcium orthophosphate deposits: Preparation, properties and biomedical applications. *Mater Sci Eng C*. **55**: 272–326.

Dubey A, Mailapalli D R. 2019. Zeolite coated urea fertilizer using different binders: Fabrication, material properties and nitrogen release studies. *Environ Technol Innov*. **16**: 100452.

Eberl D D. 2008. Controlled-Release Fertilizers Using Zeolites. US Geological Survey, Washington.

Eddarai E M, El Mouzahim M, Boussen R, Bellaouchou A, Guenbour A, Zarrouk A. 2022. Chitosan-kaolinite clay composite as durable coating material for slow release NPK fertilizer. *Int J Biol Macromol*. **195**: 424–432.

Eghbali Babadi F, Yunus R, Abdul Rashid S, Mohd Salleh M A, Ali S. 2015. New coating formulation for the slow release of urea using a mixture of gypsum and dolomitic limestone. *Particuology*. **23**: 62–67.

Elhassani C E, Essamlali Y, Aqlil M, Nzenguet A M, Ganetri I, Zahouily M. 2019. Urea-impregnated HAP encapsulated by lignocellulosic biomass-extruded composites: A novel slow-release fertilizer. *Environ Technol Innov*. **15**: 100403.

Elsayed A A A, EL-Gohary A, Taha Z K, Farag H M, Hussein M S, AbouAitah K. 2022. Hydroxyapatite nanoparticles as novel nano-fertilizer for production of rosemary plants. *Sci Hortic*. **295**: 110851.

Fellet G, Pilotto L, Marchiol L, Braidot E. 2021. Tools for nano-enabled agriculture: Fertilizers based on calcium phosphate, silicon, and chitosan nanostructures. *Agronomy*. **11**: 1239.

Fertahi S, Bertrand I, Ilsouk M, Oukarroum A, Amjoud M, Zeroual Y, Barakat A. 2020. New generation of controlled release phosphorus fertilizers based on biological macromolecules: Effect of formulation properties on phosphorus release. *Int J Biol Macromol*. **143**: 153–162.

Giroto A S, Guimarães G G F, Foschini M, Ribeiro C. 2017. Role of slow-release nanocomposite fertilizers on nitrogen and phosphate availability in soil. *Sci Rep*. **7**: 46032.

Giroto A S, Guimaraes G G F, Majaron V, Klaic R, Avansi W, Ribeiro C. 2024. Effect of urea: Hydroxyapatite composites for controlled-release fertilization to reduce P complexation in soils. *Commun Soil Sci Plant Anal*. **55**: 302–312.

Guelfi D, Nunes A P P, Sarkis L F, Oliveira D P. 2022. Innovative phosphate fertilizer technologies to improve phosphorus use efficiency in agriculture. *Sustainability*. **14**: 14266.

Guimarães G G F, Klaic R, Giroto A S, Majaron V F, Avansi W, Farinas C S, Ribeiro C. 2018. Smart fertilization based on sulfur-phosphate composites: Synergy among materials in a structure with multiple fertilization roles. *ACS Sustain Chem Eng*. **6**: 12187–12196.

Gunaratne G, Kottegoda N, Adassooriya N M, Munaweera I, Sandaruwan C, Priyadarshana G, Siriwardhana A, Madhushanka B A D, Rathnayake U, Karunaratne V. 2016. Two new plant nutrient nanocomposites based on urea coated hydroxyapatite: Efficacy and plant uptake. *Indian J Agric Sci*. **86**: 494–499.

Guo H Y, White J C, Wang Z Y, Xing B S. 2018. Nano-enabled fertilizers to control the release and use efficiency of nutrients. *Curr Opin Environ Sci Health*. **6**: 77–83.

Jarosiewicz A, Tomaszewska M. 2003. Controlled-release NPK fertilizer encapsulated by polymeric membranes. *J Agric Food Chem*. **51**: 413–417.

Jiang H, Liu J K, Wang J D, Lu Y, Zhang M, Yang X H, Hong D J. 2014. The biotoxicity of hydroxyapatite nanoparticles to the plant growth. *J Hazard Mater*. **270**: 71–81.

Kenawy E R, Seggiani M, Cinelli P, Elnaby H M H, Azaam M M. 2020. Swelling capacity of sugarcane bagasse-*g*-poly(acrylamide)/attapulgite superabsorbent composites and their application as slow release fertilizer. *Eur Polym J*. **133**: 109769.

Khan M N, Mobin M, Abbas Z K, Almutairi K A, Siddiqui Z H. 2017. Role of nanomaterials in plants under challenging environments. *Plant Physiol Biochem*. **110**: 194–209.

Klein M, Poverenov E. 2020. Natural biopolymer-based hydrogels for use in food and agriculture. *J Sci Food Agric*. **100**: 2337–2347.

Klinpituksa P, Kosaiyakanon P. 2017. Superabsorbent polymer based on sodium carboxymethyl cellulose grafted polyacrylic acid by inverse suspension polymerization. *Int J Polym Sci*. **2017**: 3476921.

Kottegoda N, Sandaruwan C, Priyadarshana G, Siriwardhana A, Rathnayake U A, Berugoda Arachchige D M, Kumarasinghe A R, Dahanayake D, Karunaratne V, Amaratunga G A J. 2017. Urea-hydroxyapatite nanohybrids for slow release of nitrogen. *ACS Nano*. **11**: 1214–1221.

Li Z W, Huang J A. 2014. Effects of nanoparticle hydroxyapatite on growth and antioxidant system in pakchoi (*Brassica chinensis* L.) from cadmium-contaminated soil. *J Nanomater*. **2014**: 470962.

Liang D S, Zhang Q, Zhang W B, Liu L X, Liang H Y, Quirino R L, Chen J, Liu M H, Lu Q M, Zhang C Q. 2019. Tunable thermo-physical performance of castor oil-based polyurethanes with tailored release of coated fertilizers. *J Clean Prod*. **210**: 1207–1215.

Liu R Q, Lal R. 2014. Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (*Glycine max*). *Sci Rep*. **4**: 5686.

Liu R Q, Lal R. 2015. Potentials of engineered nanoparticles as fertilizers for increasing agronomic productions. *Sci Total Environ*. **514**: 131–139.

Liu X M, Zhang F D, Zhang S Q, He X S, Wang R F, Fei Z B, Wang Y J. 2005. Responses of peanut to nano-calcium carbonate. *J Plant Nutr Fertil*. **11**: 385–389.

Liu Y H, Wang T J, Qin L, Jin Y. 2008. Urea particle coating for controlled release by using DCPD modified sulfur. *Powder Technol*. **183**: 88-93.

Ma J Y, Quan Z J, Sun Y B, Du J Q, Liu B. 2020. Excess sulfur and Fe elements drive changes in soil and vegetation at abandoned coal gangues, Guizhou China. *Sci Rep*. **10**: 10456.

Madanayake N H, Adassooriya N M, Salim N. 2021. The effect of hydroxyapatite nanoparticles on *Raphanus sativus* with respect to seedling growth and two plant metabolites. *Environ Nanotechnol Monit Manag*. **15**: 100404.

Madusanka N, Sandaruwan C, Kottegoda N, Sirisena D, Munaweera I, De Alwis A, Karunaratne V, Amaratunga G A J. 2017. Urea-hydroxyapatite-montmorillonite nanohybrid composites as slow release nitrogen compositions. *Appl Clay Sci*. **150**: 303-308.

Maghsoodi M R, Ghodszad L, Asgari Lajayer B. 2020. Dilemma of hydroxyapatite nanoparticles as phosphorus fertilizer: Potentials, challenges and effects on plants. *Environ Technol Innov*. **19**: 100869.

Mansouri H, Ait Said H, Noukrati H, Oukarroum A, Ben Youcef H, Perreault F. 2023. Advances in controlled release fertilizers: Cost-effective coating techniques and smart stimuli-responsive hydrogels. *Adv Sustain Syst*. **7**: 2300149.

Marchiol L, Filippi A, Adamiano A, Degli Esposti L, Iafisco M, Mattiello A, Petrussa E, Braidot E. 2019. Influence of hydroxyapatite nanoparticles on germination and plant metabolism of tomato (*Solanum lycopersicum* L.): Preliminary evidence. *Agronomy*. **9**: 161.

Mastronardi E, Tsae P, Zhang X R, Monreal C, DeRosa M C. 2015. Strategic role of nanotechnology in fertilizers: Potential and limitations. *In* Rai M, Ribeiro C, Mattoso L, Duran N (eds.) Nanotechnologies in Food and Agriculture. Springer, Cham. pp. 25–67.

Megalathan A, Kumarage S, Dilhari A, Weerasekera M M, Samarasinghe S, Kottegoda N. 2016. Natural curcuminoids encapsulated in layered double hydroxides: A novel antimicrobial nanohybrid. *Chem Cent J*. **10**: 35.

Mehmood A, Niazi M B K, Hussain A, Beig B, Jahan Z, Zafar N, Zia M. 2019. Slow-release urea fertilizer from sulfur, gypsum, and starch-coated formulations. *J Plant Nutr*. **42**: 1218–1229.

Messa L L, Faez R. 2020. Spray-dried chitosan/nanocellulose microparticles: Synergistic effects for the sustained release of NPK fertilizer. *Cellulose*. **27**: 10077–10093.

Mondal S, Pal U. 2019. 3D hydroxyapatite scaffold for bone regeneration and local drug delivery applications. *J Drug Deliv Sci Technol*. **53**: 101131.

Montalvo D, McLaughlin M J, Degryse F. 2015. Efficacy of hydroxyapatite nanoparticles as phosphorus fertilizer in Andisols and Oxisols. *Soil Sci Soc Am J*. **79**: 551–558.

Ranjbar S, Ramezanian A, Rahemi M. 2020. Nano-calcium and its potential to improve 'Red Delicious' apple fruit characteristics. *Hortic Environ Biotechnol*. **61**: 23–30.

Rashidzadeh A, Olad A. 2014. Slow-released NPK fertilizer encapsulated by NaAlg-*g*-poly(AA-*co*-AAm)/MMT superabsorbent nanocomposite. *Carbohydr Polym*. **114**: 269–278.

Rather R A, Bhat M A, Shalla A H. 2022. An insight into synthetic and physiological aspects of superabsorbent hydrogels based on carbohydrate type polymers for various applications: A review. *Carbohydr Polym Technol Appl*. **3**: 100202.

Rop K, Karuku G N, Mbui D, Michira I, Njomo N. 2018. Formulation of slow release NPK fertilizer (cellulose-graft-poly(acrylamide)/nano-hydroxyapatite/soluble fertilizer) composite and evaluating its N mineralization potential. *Ann Agric Sci*. **63**: 163–172.

Rop K, Karuku G N, Mbui D, Njomo N, Michira I. 2019. Evaluating the effects of formulated nano-NPK slow release fertilizer composite on the performance and yield of maize, kale and capsicum. *Ann Agric Sci*. **64**: 9–19.

Rop K, Mbui D, Karuku G N, Michira I, Njomo N. 2020. Characterization of water hyacinth cellulose-*g*-poly(ammonium acrylate-*co*-acrylic acid)/nano-hydroxyapatite polymer hydrogel composite for potential agricultural application. *Results Chem*. **2**: 100020.

Sajadinia H, Ghazanfari D, Naghavii K, Naghavi H, Tahamipur B. 2021. A comparison of microwave and ultrasound routes to prepare nano-hydroxyapatite fertilizer improving morphological and physiological properties of maize (*Zea mays* L.). *Heliyon*. **7**: e06094.

Sattar B, Ahmad S, Daur I, Hussain M B, Ali M, ul Haq T, Arif M, Bakhtawer M. 2021. Bioactive-sulfur coated diammonium phosphate improves nitrogen and phosphorus use efficiency and maize (*Zea mays* L.) yield. *J Environ Agric Sci*. **23**: 23–29.

Seydmohammadi Z, Roein Z, Rezvanipour S. 2020. Accelerating the growth and flowering of *Eustoma grandiflorum* by foliar application of nano-ZnO and nano-$CaCO_3$. *Plant Physiol Rep*. **25**: 140–148.

Shavit U, Reiss M, Shaviv A. 2003. Wetting mechanisms of gel-based controlled-release fertilizers. *J Control Release*. **88**: 71–83.

Shaviv A. 2001. Advances in controlled-release fertilizers. *Adv Agron*. **71**: 1–49.

Shen Z Y, Shen W Y, Chen M H, Shen J, Cai W J, Zeng Y. 2002. Mitochondria, calcium and nitric oxide in the apoptotic pathway of esophageal carcinoma cells induced by As_2O_3. *Int J Mol Med*. **9**: 385–390.

Shilo S, Aronis A, Komarnitsky R, Tirosh O. 2003. Selenite sensitizes mitochondrial permeability transition pore opening *in vitro* and *in vivo*: A possible mechanism for chemo-protection. *Biochem J*. **370**: 283–290.

Sim D H H, Tan I A W, Lim L L P, Hameed B H. 2021. Encapsulated biochar-based sustained release fertilizer for precision agriculture: A review. *J Clean Prod*. **303**: 127018.

Sousa H R, Lima I S, Neris L M L, Silva A S, Santos Nascimento A M S, Araújo F P, Ratke R F, Silva D A, Osajima J A, Bezerra L R, Silva-Filho E C. 2021. Superabsorbent hydrogels based to polyacrylamide/cashew tree gum for the controlled release of water and plant nutrients. *Molecules*. **26**: 2680.

Stanley N, Mahanty B. 2020. Preparation and characterization of biogenic $CaCO_3$-reinforced polyvinyl alcohol-alginate hydrogel as controlled-release urea formulation. *Polym Bull*. **77**: 529–540.

Subbaiya R, Priyanka M, Selvam M M. 2012. Formulation of green nano-fertilizer to enhance the plant growth through slow and sustained release of nitrogen. *J Pharm Res*. **5**: 5178–5183.

Subramanian K S, Thirunavukkarasu M. 2017. Nano-fertilizers and nutrient transformations in soil. *In* Ghorbanpour M, Manika K, Varma A (eds.) Nanoscience and Plant-Soil Systems. Springer, Cham. pp. 305–319.

Tang H Y, Wang X B, Wang C Y, He T T, Wang J C. 2024. Design of a novel multifunctional soil conditioner based on Fe-modified hydroxyapatite/polydopamine/amino carbon nanotubes. *Colloids Surf A: Physicochem Eng Aspects*. **687**: 133518.

Teodorescu M, Lungu A, Stanescu P O, Neamt C. 2009. Preparation and properties of novel slow-release NPK agrochemical formulations based on poly(acrylic acid) hydrogels and liquid fertilizers. *Ind Eng Chem Res*. **48**: 6527–6534.

Trenkel M E. 2010. Slow- and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Efficiency in Agriculture. International Fertilizer Industry Association, Paris.

Valle S F, Giroto A S, Guimarães G G F, Nagel K A, Galinski A, Cohnen J, Jablonowski N D, Ribeiro C. 2022. Co-fertilization of sulfur and struvite-phosphorus in a slow-release fertilizer improves soybean cultivation. *Front Plant Sci*. **13**: 861574.

Vishwakarma K, Upadhyay N, Kumar N, Tripathi D K, Chauhan D K, Sharma S, Sahi S. 2018. Potential applications and avenues of nanotechnology in sustainable agriculture. *In* Tripathi D K, Ahmad P, Sharma S, Chauhan D K, Dubey N K (eds.) Nanomaterials in Plants, Algae, and Microorganisms. Academic Press, London. pp. 473–500.

Wang H G, Pathan N, Ethell I M, Krajewski S, Yamaguchi Y, Shibasaki F, McKeon F, Bobo T, Franke T F, Reed J C. 1999. Ca^{2+}-induced apoptosis through calcineurin dephosphorylation of BAD. *Science*. **284**: 339–343.

Wang M, Chen L, Chen S B, Ma Y B. 2012. Alleviation of cadmium-induced root growth inhibition in crop seedlings by nanoparticles. *Ecotoxicol Environ Saf*. **79**: 48–54.

Wang Y X, Ngo H H, Guo W S. 2015. Preparation of a specific bamboo based activated carbon and its application for ciprofloxacin removal. *Sci Total Environ*. **533**: 32–39.

Wilske B, Bai M, Lindenstruth B, Bach M, Rezaie Z, Frede H G, Breuer L. 2014. Biodegradability of a polyacrylate superabsorbent in agricultural soil. *Environ Sci Pollut Res*. **21**: 9453–9460.

Xiong L, Wang P, Hunter M N, Kopittke P M. 2018a. Bioavailability and movement of hydroxyapatite nanoparticles (HA-NPs) applied as a phosphorus fertiliser in soils. *Environ Sci: Nano*. **5**: 2888–2898.

Xiong L, Wang P, Kopittke P M. 2018b. Tailoring hydroxyapatite nanoparticles to increase their efficiency as phosphorus fertilisers in soils. *Geoderma*. **323**: 116–125.

Yoon H Y, Lee J G, Esposti L D, Iafisco M, Kim P J, Shin S G, Jeon J R, Adamiano A. 2020. Synergistic release of crop nutrients and stimulants from hydroxyapatite nanoparticles functionalized with humic substances: Toward a multifunctional nanofertilizer. *ACS Omega*. **5**: 6598–6610.

Zhang M X, Yang J S. 2021. Preparation and characterization of multi-functional slow release fertilizer coated with cellulose derivatives. *Int J Polym Mater Polym Biomater*. **70**: 774–781.

Zhao C C, Gupta V V S R, Degryse F, McLaughlin M J. 2017. Effects of pH and ionic strength on elemental sulphur oxidation in soil. *Biol Fertil Soils*. **53**: 247–256.

Zhong K, Lin Z T, Zheng X L, Jiang G B, Fang Y S, Mao X Y, Liao Z W. 2013. Starch derivative-based superabsorbent with integration of water-retaining and controlled-release fertilizers. *Carbohydr Polym*. **92**: 1367–1376.