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Mini Review

The Utilization of Hydroxyapatite as Green Fertilizer Increasing Soil Fertility

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Abstract

Besides hydroxyapatite (HA) being utilized in bioengineering because it is similar to the component of bone and teeth, HA is also optimized as a fertilizer and a coating seed to deliver micro and macronutrients. The other benefits are to provide the phosphorus element for supporting the growth of a plant and to avoid depleting the P element in soil. HA can be obtained from natural waste (shells and bone) that have to be treated by various methods. One of them is the wet precipitation method which results in many products and just needs an organic solvent.

Introduction

In some research, hydroxyapatite (HA or ($Ca_{10}(PO_4)_8(OH)_2$)) has been occasionally applied in the medical field. Because phosphor and calcium as their main components, hydroxyapatite is installed on the implant which accelerates the healing of bone. Fortunately, some researchers have also used some wastes like animal bones, shells, scales, and limestone as sources of calcium. This material is also fabricated and combined with the other polymers to be made the scaffold [1]. Through many methods such as the hydrothermal, precipitation method, sol-gel, etc., hydroxyapatite can be produced within the controlled parameters (temperature, aging time, pressure, pH).

Although hydroxyapatite is frequently utilized in biomaterial engineering, it is also found in a farming products, as fertilizer. Phosphorus is one of the fundamental elements in fertilizer. Conversely, based on data, the quantity of phosphorus has depleted and will be no P element in the soil in 2050 [2]. The needed property of phosphorus-based fertilizer is solubility. The change of HA particle size and optimization of microorganisms are engineered properties that are controlled on phosphate calcium material to increase phosphor solubility. Bacillus licheniformis have been a mediator to increase the solubility of phosphorus because of produced gluconic acid [3]. This review article emphasizes the utility and mechanism of hydroxyapatite as fertilizer and others that support the agriculture field.

Discussion

Fabrication of hydroxyapatite through wet precipitation method and the utilization of natural resources

Hydroxyapatite (HA) is a kind of bioceramic which component has similarity to the component of bone and teeth. However, there is a difference between hydroxyapatite and bone apatite. The impurity that substitutes calcium (Ca) in the structure apatite indicates the bone apatite. Furthermore, hydroxyapatite has a ratio of Ca and P calculated at 1.67 while the bone, tooth enamel, and dentin have a ratio of Ca and P 1.71, 1.63, and 1.61 respectively [4].

For fabrication of HA, needs a simple technique and produces more quantity. Therefore, of many methods, wet precipitation is a method underlying the fabrication of HA. To carry it out, some parameters like pH, stirring temperature, precursors (calcium and phosphate), stirring time, and calcination need to be controlled [5]. The steps based on the wet precipitation method

a) React precursors between calcium and phosphate
b) The solution is stirred up constantly
c) Solution is precipitated and colloidal HA
d) Dried and calcined at 900~1200°C [5].

Materials that are used as a precursor can be obtained from natural resources. Previous studies have reported that natural wastes such as shells, bones, and eggshells are used as calcium precursors or calcium carbonate sources. Through calcination treatment, it is transformed to be calcium oxide (Equation 1). It will be mixed with the precursor of phosphorus. The presence of functional carbonate molecule characterized by Fourier transform infrared was detected at 852.21 cm^{-1} while the presence of calcium oxide was detected at 709.43 cm^{-1} [1].

$$CaCO_{3\,(s)} \rightarrow CaO_{\,(s)} + CO_{2\,(g)} \qquad (1)$$

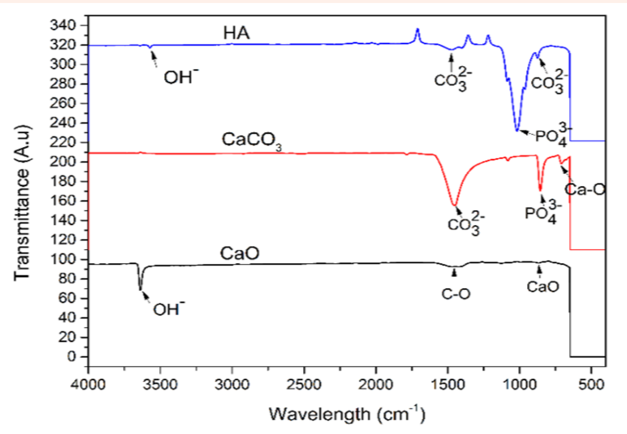

Figure 1: Wavelength of CaO, $CaCO_3$, and HA characterized by FTIR [1].

The utilization of hydroxyapatite as fertilizer

Various kinds of waste have been reported to be used as nutrient sources for the growth of an organism including plants. Utilization of organic-rich nutrient components can reduce production costs and increase the yield of agricultural production [6,7]. Hydroxyapatite is a source of green fertilizer that can be produced from various types of waste, such as shellfish, shell egg, and fish bone (Figure 1). Hydroxyapatite is a compound that contains some essential nutrients needed by plants such as nitrogen and phosphorus [8].

Nitrogenous and urea nano-hydroxyapatite fertilizers are reported to increase the growth of the broad bean *(Vicia Faba L.)*. This was because the nitrogen content contained in the fertilizer was able to increase the production of chlorophyll in the leaves of this plant. An adequate amount of nitrogen causes plants to be able to synthesize chlorophyll properly so that the growth rate of plants will be increased. Chlorophyll is one of the important factors in plant growth, plants are highly dependent on the process of photosynthesis which involves chlorophyll to produce energy for the division and growth of cells. The most optimal concentration of nitrogenous and urea nano-hydroxyapatite-based fertilizer was 75 ppm. Besides being able to increase plant growth, this fertilizer was also reported to increase metabolites and yields of cultivated plants [9].

Hydroxyapatite can also be applied as a coating agent on seeds which will help the seed germination process. This is because the addition of hydroxyapatite-based seed coatings was reported to be able to increase the delivery of micronutrients and macronutrients to seed embryos. This coating was reported to be able to increase the germination of corn (Zea mays) seeds by 69%. Coating the seeds increases the delivery of various nutrients such as phosphorus, nitrogen, and zinc. Macro and micronutrient elements are needed for the growth of a plant, such as forming chlorophyll, producing energy in the form of ATP, forming DNA, and so on [10].

Other studies tested the availability of element P contained in hydroxyapatite at certain soil pH levels. Fertilizers based on hydroxyapatite nanoparticles were known to be suitable for application to soils with low or acidic pH. On acidic soils, the fertilizer is effective in increasing plant biomass by 30%. Meanwhile, at high pH (8), the availability of P in the fertilizer decreased. Thus, the fertilizer is very suitable to be applied to agriculture on acidic soils. This can be used as a solution to increase the productivity of land with low pH. This is because agriculture on acidic soils like peatland is often hindered by the low availability of nutrients in the soil so that they cannot be absorbed by plants to support their growth [11,12]. Furthermore, the presence of microorganism Bacillus licheniformis helps P solubility in order to absorb by plant. The bacteria will produce gluconic acid when bacteria contacts with the phosphorus material, like HA [3].

Conclusion

The plant needs micro and macro-nutrients for growing cells and producing energy via photosynthesis. However, the plant has barriers, like the limit of nutrients in the soil, such as P and N, and the pH, and soil acidity. Therefore, the plant utilizes fertilizer and bioengineering techniques should be applied (in this case, coating). As a bioceramic containing calcium and phosphorus, HA is potentially used to fulfill plant's nutrients. HA can be fabricated by various methods and using types of waste (shells and bone). Calcium carbonate contained in shells can be transformed into calcium oxide. It is mixed with phosphorus through chemical and physical processes considering temperature, pH of the solution, stirring time, and aging time.

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