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Processing and Characterization of Nano Hydroxyapatite from Bio wastes as a Fertilizer for Wheat and Soybean

Presented by

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List of Abbreviations

Å	Angstrom
APP	Ammonium Polyphosphate
β	Beta
Ba	Barium
BvHAp	Hydroxyapatite from bovine bone waste
β-TCP	Beta-tricalcium phosphate
C	Concentration
°C	Degree Celsius
Ca	Calcium
CCD	Charge-coupled device
CES	Chicken eggshells
Cr	Chrome
CSP	Concentrated Superphosphate
DAHP	3-deoxy-D-arabino-heptulosonate 7-phosphate
DAP	Di-ammonium phosphate
DES	Duck eggshells
DLS	Dynamic light scattering
DNA	Deoxyribonucleic acid
E	Eggshell
E-HAp	Hydroxyapatite from Eggshell
EDTA	Ethylene di-amine tetra-acetic acid
EDX	Energy-dispersive X-ray spectroscopy
F	Fish bone
F-HAp	Hydroxyapatite from fish bone
FWHM	Full width at half maximum
FTIR	Fourier Transform Infra-Red spectroscopy.
h	Hour
HR-TEM	High resolution transmission electron microscope
HAp	Hydroxyapatite.
ICP-AES	Inductively coupled plasma– atomic emission spectroscopy
K	Potassium
KBr	Potassium bromide

l	Path length
Li	Lithium
LSD	Least significance difference
M	Molar
MAP	Mono-ammonium phosphate
Mg	Manganese
MN	Mineral nitrogen
MW	Molecular weight
µL	Microliter
MSCs	Mesenchymal stem cells
MPa	Megapascal Pressure Unit
nHAp	Nano-hydroxyapatite
NUE	Nitrogen utilization efficiency
N-P	Nitrogen- Phosphorus
P	Phosphorus
pH	Power of hydrogen.
RNA	Ribonucleic acid
rpm	Rotation per minute
SP	Superphosphate
SRF	Slow release fertilizer
SEM	Scanning electron microscopy
TEM	Transmission Electron Microscopy.
TG/DTA	Thermo-gravimetry/Differential Thermal Analyzer.
TGA	Thermo gravimetric analysis
TSP	Triple-superphosphate
UV	Ultra-violet
Vis.	Visible
XRD	X-Ray Diffraction.
XRF	X-ray fluorescence
ε	Molar absorptivity
θ	Theta
λ	Wavelength

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Abstract

Plants require many nutrients and minerals to survive, which are either supplied from the soil or by fertilizer. Phosphorus is one of these minerals, which helps plants to form a set of buds and fruiting. The use of conventional phosphate fertilizers causes environmental pollution due to over-fertilization. Because of its large size, the plant cannot absorb all the amount of fertilizer and remains part of it in the soil has not been absorbed and less diffused. If too much phosphate fertilizer is used on the soil, excess phosphorus can easily find its way into water networks through storm and plumbing drains. Herbs and plant leaves grown in the soil with excess phosphorus will release phosphorus into the water, leading to outbreaks of algae, bacteria and water pollution, and resulting in poor soil and plant quality. For these explained reasons, many researchers found the importance of nano-hydroxyapatite as a potential fertilizer in improving the efficiency of phosphorus based on the hypothesis that nano-sized particles can potentially move in the soil and reach the plant roots through the mass flow of soil water to roots created by transpiration. So the usage of nano-phosphorus fertilizer can be a beneficial and safe way to improve soil fertility without causing any environmental pollution. Hydroxyapatite **[HAp, $Ca_{10}(PO_4)_6(OH)_2$]** is one of the widely used bio-ceramics in different fields especially in medical and agricultural applications. Hydroxyapatite can be naturally prepared from biological wastes such as fish bones, bovine bones, coral reefs and egg shells, not only from the economical point of view but also as a friend of the environment.

Objective of the current work:

First: preparation of nano-hydroxyapatite from fish bone and eggshell:

1. Preparation of nano-hydroxyapatite from fish bone: by extracting it from the thorns using sodium hydroxide, acetone and concentrated hydrochloride solution to dispose of the organic matter found in the fish bone. The sample is then subjected to a high temperature 1100 °C to ensure that no residual organic matter only the inorganic material representing nano-hydroxyapatite remains.

2. Preparation of nano-hydroxyapatite from egg shell: As we know that the basic component of the eggshell calcium carbonate ($CaCO_3$) when exposure to eggshell at a high temperature of 900 °C turns calcium carbonate into calcium oxide (CaO) and rising carbon dioxide (CO_2). Calcium oxide is then reacted with ortho-phosphoric acid solution by the wet chemical precipitation method. The egg husk here represents a source of calcium, eventually producing the nano-hydroxyapatite.

Second: Characterization of hydroxyapatite produced from both samples (from fish bone and egg shell) by biophysical techniques:

1. Infrared Spectroscopy (FTIR): The presence of functional groups of hydroxyapatite, OH^{-1} and PO_4^{-3}groups, were confirmed in both samples.
2. X-ray diffraction (XRD): Confirmed that the chemical structure of both samples is pure hydroxyapatite without any chemical impurities. The size of the crystallites could be calculated by using Scherrer equation which confirmed that both samples were in the size of the nanostructures 64.8 ± 0.36 nm in case of fish bone sample and 46.3 ± 0.32 nm in case of egg shell sample.
3. Transmission electron microscope (TEM): Used in the study of morphology and size determination and explained that the particles of both egg shell and fish bone samples in the size of nanostructures.

This study showed that not only fish bone but also egg shells can be used as bio-wastes for high quality nano-hydroxyapatite production with ideal properties for medical and agricultural applications.

Third: the use of nano-hydroxyapatite product in the field of agriculture as a phosphate fertilizer for the cultivation of some important economic plants such as wheat and soybean:

1. Application of nano-hydroxyapatite fertilizer for soybean cultivation: The current results showed significant differences in the growth rate of the use of hydroxyapatite produced from fish bone (F-HAp) and hydroxyapatite produced from eggshell (E-HAp) fertilizers compared with regular phosphorus fertilizer. The data obtained showed that the rate of

growth of plants treated with nanoparticles was 1.88 times greater than the rate treated by traditional phosphate. Analysis of micronutrients revealed that the concentration of nitrogen (N), phosphorus (P) and potassium (K) in plants treated with F-HAp fertilizer was significantly greater than that of plants treated with regular phosphate with 1.21, 1.32 and 1.17, respectively.

2. Application of nano-hydroxyapatite fertilizer for growing wheat:

   The weight of wheat spikes when using nano-hydroxyapatite from fish bone was 2.61 times higher than regular phosphorous fertilizer. Also when using nano-hydroxyapatite fertilizer, which is equivalent to 50% of the amount used in the case of conventional phosphorus fertilizer, the ratio of phosphorus was 1.21 and 1.06 times in the case of nano-hydroxyapatite from fish bone and eggshell, respectively.

From this study it was found that fish bones and eggshells can be used as biological waste for high quality HAp synthesis with properties for agricultural applications such as nano phosphorous fertilizer for soybeans and wheat. Data obtained indicate that both F-HAp and E-HAp were able to promote soybean and wheat productions compared to traditional phosphorus fertilizers, which needed further research in a larger area of the field.

Keywords: hydroxyapatite, egg shells, fish bone, X-ray diffraction, fertilizers.

Chapter (1)

Introduction and review of literature

1.1. Introduction

Nanotechnology is defined as the science which deals with material at the scale of 1 billionth of a meter (i.e., 10^{-9}m = 1 nm), and is also the study of manipulating matter at the atomic and molecular range. Nanoparticle (or nano-powder or nano-crystal or nano-cluster) is particulate substance with at least one dimension that is below 100 nm. Nanoparticle research is presently a zone of powerful scientific research, because of an extensive diversity of possible applications in biomedical, optical, agricultural, and electronic fields. Nanoparticles are of great scientific attention as they are excellently a bridge between bulk materials and atomic or molecular structure [1].

Nowadays nanotechnology providing different nano devices and nano material which having a unique role in agriculture such as nano biosensors to detect moisture content and nutrient status in the soil and also applicable for site specific water and nutrient management, Nano-fertilizers for efficient nutrient management, Nano-herbicides for selective weed control in crop field, Nano-nutrient particles to increase seed vigor, Nano-pesticides for efficient pest management. alginate/ chitosan nano-particles can be used as herbicide carrier material specially for herbicide such as paraquat [2]. Nano herbicides are effective in weed management [3]. Hence, nanotechnology have greater role in crop production with environmental safety, ecological sustainability and economic stability. The nano-particles produced with the help of nanotechnology can be exploited in the value chain of entire agriculture production system [4].

Nano-fertilizers “Nano fertilizers are synthesized or modified form of traditional fertilizers, fertilizers bulk materials or extracted from different vegetative or reproductive parts of the plant by different chemical, physical, mechanical or biological methods with the help of nanotechnology used to improve soil fertility, productivity and quality of agricultural produces. Nanoparticles can be made from fully bulk materials [5]. At nano scale physical and chemical properties are differ than bulk material .Similarly reported [6], Rock phosphate if use as nano form it may increase availability of phosphorus to the plant because direct application of rock phosphate nano particles on the crop may prevent fixation in the soil similarly there is no silicic acid, iron