PREPARATION AND CHARACTERIZATION OF NUTRIENT RICH NANOPARTICLES / COMPOSITES FOR AGRICULTURAL APPLICATIONS

Munaweera Thanthrige Imalka Shanika Munaweera

(09/8093)

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Department of Chemical & Process Engineering

University of Moratuwa

Sri Lanka

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Declaration

I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

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M. T. I. S. Munaweera Date: 7/7/2011

The above candidate has carried out research for the M. Phil thesis under our supervision.

UOM Verified Signature

Prof. V. Karunarathne Date: 7/7/2011

Supervisor

UOM Verified Signature

Dr. N. S. Kottegoda Date: 07/07/2011

Supervisor

UOM Verified Signature

Dr. F. M. Ismail Date: 9/07/2011

Supervisor

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Abstract

The work describes a novel strategy for controlled and sustained release of plant nutrients nitrogen (N), phosphorous (P) and potassium (K) into soil. In the study two nano systems, (a) inorganic inner nano-core consisting of macronutrient nanoparticles (b) a natural cellulose based outer core containing micro / nano porous cavities were used in order to obtain slow and sustained release of nutrients. Hydroxyapatite (HA) nanoparticles were synthesized, surface modified using urea and characterized using PXRD, SEM / EDX, AFM, FTIR and TGA / DTA. Urea modified HA nanoparticles dispersion and saturated potassium chloride solution were separately pressurized into the cavities present in *Gliricidia sepium,* a soft wood stem, under a pressure of 9 bar. N, P and K release behavior of the nanofertilizer composition was studied using soil from three elevations in Sri Lanka (pH 4.2, 5.2 and 7) and the release properties were compared with that of a commercial fertilizer composition. The release properties of the nanofertilizer show a slow and sustained release. In general, at all pH values, even on day 32, the remaining N to be released in the nanofertilizer was about 20% and there was no more N to be released in the commercial fertilizer. A similar trend shows for K release and at all pH values the remaining K to be released in nanofertilizer after 40 days was about 15% while there was no more K to be released in the commercial fertilizer. The solubility of P of in the nanofertilizer system was higher than the P release of the commercial fertilizer.

A model was developed for the solubility of bulk HA / HA nanoparticles. The solubility of HA in terms of soluble phosphate (PO_4^{3-}) can be expressed by an equation,

$$\left[PO_4^{3-}\right]_{total} = \left(\frac{K_{sp}}{K_w}\right)^{\frac{1}{8}} \times \frac{\left[\left(a_{H^+}\right)^{\frac{1}{3}} + \frac{\left(a_{H^+}\right)^{\frac{4}{3}}}{K_3} + \frac{\left(a_{H^+}\right)^{\frac{7}{3}}}{K_2K_3} + \frac{\left(a_{H^+}\right)^{\frac{10}{3}}}{K_1K_2K_3}\right]^{\frac{3}{8}}}{\left[\frac{3}{5} \times e^{\left|\frac{1}{2.303}\right| Z_{Ca^{2+}}\left|^2 \times 0.509 \times \sqrt{I}\right|}\right]^{\frac{5}{8}}}$$

From pH 3 to 4 and pH 4.5 to 6 the decrement of log value of total soluble phosphate concentration per unit pH is 11.8 and 3.03, respectively, when the ionic strength of the soil solution is between 12 to 110 mol kg^{-1} according to the Ostwald and Freundlich equation, the solubility of phosphate can be increased by reducing the size of HA, that is, by using HA nanoparticles.

Key words: slow release, macronutrients, fertilizer, nanoparticles, wood

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LIST OF ABBREVIATIONS

Abbreviation	Description
Å	Angstrom
AFM	Atomic Force Microscope
ATR	Attenuated Total Reflectance
AES	Auger Electron Spectroscopy
CRF	Controlled Release Fertilizer
DHA	Defective Hydroxyapatite
DNA	Deoxyribonucleic Acid
$	Dollar
EBSD	Electron Back Scatter Diffraction
EDS	Electronic Data Systems
EDX	Energy Dispersive X-ray analysis
EDS	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
g	gram
$g\ kg^{-1}$	gram per kilogram
HP	Hewlett-Packard
HA	Hydroxy Apatite
IBM	International Business Machines
ICDD	International Centre for Diffraction Data
kg	kilogram
KHz	Kilo Hertz
kV	Kilo Volts
$mg\ kg^{-1}$	milligram per kilogram
$mg\ l^{-1}$	milligram per liter
N/ha	Nitrogen per hectare
$N\ ha^{-1}\ day^{-1}$	Nitrogen per hectare per day

NBP	Nanotechnology Based Pesticides
NUE	Nitrogen Utilization Efficiency
Pa	Pascal
PSCU	Polymer coated Sulphur Coated Urea
PDF	Portable Document Format
PXRD	Powder X-ray Diffraction
SEM	Scanning Electron Microscope
STM	Scanning Tunneling Microscope
SSNM	Site Specific Nutrient Management
SRF	Slow Release Fertilizer
SLS	Sri Lanka Standards
SCU	Sulphur Coated Urea
TA	Thermal Analysis
TGA	Thermo Gravimetric Analysis
TCP	Tri Calcium Phosphate
US	United State
WDS	Wavelength-Dispersive X-ray Spectroscopy
XPS	X ray Photoelectron Spectroscopy

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