

# Fabricating Novel Nanoproducts for Their Use as Fertilizer

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## Abstract

Fertilizer resources, especially phosphates and potassium are fast getting depleted. They also have poor use efficiency, burden farm economy, and pollute entire ecosystem. It was, therefore aimed to develop novel process and materials using nanotechnology. Novel process (patents applied) of nanofabrication and beneficiation of Rock Phosphate ore led to heavy-metal free phosphate-rich minerals and Zn-products. Novel P and Zn nanoproducts (patents applied) ensured supply of nutrients in plant available forms, and in conformity to environmental quality.

## Keywords

Beneficiation of phosphate rock, Clay mineral, Fertilizer, Kaolin, Nanofabrication process, Nanofertilizer, Nanomaterials, Nano-P, Nano-Zn, Phosphate rock

## Introduction

Fertilizer use to supplement nutrient requirement of plants is steadily rising ever since its utility was demonstrated by Justus von Liebig in 1847. However, global fertilizer consumption during 1950-2013 has grown at alarming pace, but return of crop yield per unit of fertilizer-use in world's major agricultural countries has been steadily falling [1]. The situation is further aggravated because phosphorus and potassium containing fertilizer resources are increasingly becoming scarce [2] threatening global food and nutrition security.

Existing fertilizers are known to cause soil acidity, damage soil carbon profile, harm beneficial micro-flora, weather clay minerals [3], and accumulate heavy metals (e.g., P fertilizers [4]). Another key problems of existing fertilizer materials are that most of them are salts consisting of one component of plant-nutrient ion(s), while counter component is not very useful or, toxic (e.g., muriate of potassium that contains Cl<sup>-</sup> [5]). They thereby make irreparable damage to soils and food-quality, and as a consequence detrimental to human health. Such scenario calls for systemic fabrication of materials in such manner that they supply plant-nutrient ions in plant-available forms and comply with environmental quality for which nanotechnology is indispensable [6].

## Nanofabrication process

Developing a nanofabrication process that would be simple, energy efficient and do not burden toxic load on environment is prerequisite to manufacture novel nanomaterials for their use as fertilizer and beyond it. Current industry-focused processes of nanofabrications or manufacturing nanoproducts involve physical and chemical vapour deposition, laser ablation, arc discharge, lithography for nano-deposition or nano-machining of atoms, molecules, compounds or

structures, nanoimprinting, and similar techniques. These processes are often complex, may require highly sophisticated reactors, and energy guzzling with small output potential. They work in closed system, and thereby environmental disposal issues are easy to handle. In contrast, nanofabrication process and nanoproducts focusing agricultural use must be affordable to farmers as amount of material requirement is gigantic, and must conform to the environment and health issues as agriculture and forests function in open system with little control over the fate of the material.

In view of it, a novel process of nanofabrication involving plant-nutrient ions and selected clay mineral (as receptacle) was developed [7]. The process involved breakdown of bulk-form of phyllosilicate clay-minerals along the cleavage planes by physical top-down method to nano-form. This was followed by transportation of desired ion/ ion pair from solid source material to liquid phases and then intercalating them in group or, in sheet form into inter-lattice positions along 001 planes or, on broken bond sites. To avoid coagulation/ aggregate formation, the resultant product was charged. The uniqueness of the invention is use of clay-minerals as receptacle for intercalating desired ions in sheet form. The clay minerals were used because they are known for their role in genesis of life on Earth and evolution of higher animals and also because they supply and control plant nutrients in soil system and commonly available [8].

### Beneficiation of Phosphate Rock

More than 97 percent of the world's phosphate fertilizers are produced from Phosphate Rock, which might get depleted in two decades. All Phosphate Rocks, and products derived from them contain high amounts of heavy metals (e.g., Cd, Cr, Pb, Sb, V, Zn, and Cu), and radioactive elements (e.g., U, and Th) [4]. A novel beneficiation process was developed aiming separation of phosphorous-minerals from Phosphate Rock by physical breakdown of large rock materials into smaller (sand size) parts accompanied by screening, and followed by sink-or-float separation of heavy-metal free phosphorous-minerals from the sand size ore using a chemical that does not dissolve phosphorous and can be used several times. The phosphorous-rich materials segregated by this process contained 6.6-19.5 percent of elemental phosphorous (P) equivalent to 15.12-44.68 percent of phosphorous pentoxide. The process is superior to conventional processes, because: (i) it is simple physical segregation, (ii) eliminates enrichment stage to save energy and reduce costs, (iii) environment friendly because there is no soluble-P waste, and (iv) the segregated phosphorous-rich raw materials are free from toxic heavy metals and radionuclides ensuring that the derived products are free from such contaminants [9].

### Novel nano products

Nanomaterials containing phosphate [10] and zinc [11] plant-nutrient ion(s) on clay-mineral receptacles were fabricated in such manners that resultant materials would release nutrient ions in plant-available forms, and would be compliant to environmental safety and farmers' affordability.

### Nano-phosphorous

Fabrication process of nano-phosphorous products

involves intercalating phosphate ion ( $\text{PO}_4^{3-}$ ) in kaolin clay mineral. The final product was dried and stored in sterilized container. If the nanoproduct is applied to soil as fertilizer, it would release either phosphate ions ( $\text{PO}_4^{3-}$ ), or get converted to hydrogen phosphate ions ( $\text{HPO}_4^{2-}$ ) or dihydrogen phosphate ions ( $\text{H}_2\text{PO}_4^-$ ) due to presence of water in soil environment. All three forms are available to plants, and the release of phosphate ion will be through diffusion process. Advantage of the nanoproducts over conventional fertilizers is that in the nanoproducts P is readily available, and does not contain heavy metals and other contaminants. As the P resources are likely to be depleted in a few decades and costs of environmental clean-up from eutrophication is escalating, there is no escape route, but to stop agronomic practices of applying P fertilizers in amounts ~20-80 times than plant can remove. The present nanoproduct therefore, is likely to be a viable alternative to sustain agricultural production. The nanoproducts were characterized by Fourier Transformed Infra-red Spectroscopy, Scanning Electron Microscopy (SEM) and SEM-Energy Dispersion Spectroscopy, and Transmission Electron Microscopy.

### Nano-zinc

Zinc (Zn) deficiency is wide spread in soils of the world, and it is acute in the fifty percent arable soils in India. Conventional zinc fertilizers do not adequately respond to the demands of plants over time and space. Four advanced Zn nano-materials were developed using kaolin and smectite clay-minerals as receptacles. Subsequently, they were embedded into a polymer matrix. The products contained zinc in plant available forms ( $\text{Zn}^{2+}$ ), and were suitable for soil application. The nanoproducts were characterized by: (i) basal spacing on intercalation of  $[\text{Zn}_6(\text{OH})_{12}]^{12+}$  by X-ray Diffraction, (ii) identification of structural groups by Fourier Transformed Infra-red Spectroscopy, (iii) morphology by the Scanning Electron Microscopy (SEM), (iv) elemental composition by the SEM-Energy Dispersion Spectroscopy (SEM-EDS), and (v) size of nanoproducts by the Transmission Electron Microscopy.

## Conclusion

Many existing commercial fertilizer materials have poor use efficiency and unwanted pollutants or counterparts in salts causing environmental load and detrimental to human health. Therefore they must be replaced by the novel materials – preferably in nanoform – that hold and release plant-available forms of nutrients. These objectives were attained by inventing nanofabricating process in accordance to farming requirements and segregating heavy metal free P-containing minerals from Rock Phosphate ore, and by inventing P and Zn containing nano-products in clay mineral receptacles so that they are biosafe.

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