Science of the Total Environment 514 (2015) 131–139

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Potentials of engineered nanoparticles as fertilizers for increasing agronomic productions

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HIGHLIGHTS

- Urgent need for new fertilizer to enhance crop productivity & environmental quality
- Some engineered nanomaterials show beneficial effects on plants
- These nanomaterials are promising candidates for nanofertilizer development
- Macronutrient nanofertilizers have high research priority

ARTICLE INFO

Article history:
Received 10 November 2014
Received in revised form 28 January 2015
Accepted 29 January 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Nanofertilizer
Nanoparticle
Nanomaterial
Macronutrient
Micronutrient
Agriculture
Environment

ABSTRACT

Development and application of new types of fertilizers using innovative nanotechnology are one of the potentially effective options of significantly enhancing the global agricultural productions needed to meet the future demands of the growing population. Indeed, the review of available literature indicates that some engineered nanomaterials can enhance plant-growth in certain concentration ranges and could be used as nanofertilizers in agriculture to increase agronomic yields of crops and/or minimize environmental pollution. This article summarizes this type of nanomaterials under four categories: macronutrient nanofertilizers, micronutrient nanofertilizers, nutrient-loaded nanofertilizers, and plant-growth-enhancing nanomaterials. Each category is discussed respectively with reference to nanomaterials' chemical composition, particle size, concentrations applied, benefited plant species, plant incubation methods, and plant-growth enhancement aspects and the rates. The importance, research directions, and research requirements of each nanofertilizer category for achieving sustainable agriculture are also specifically examined. Finally, this review suggests that development of N and P macronutrient nanofertilizers is a high research and development priority both for food production and environmental protection.

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http://dx.doi.org/10.1016/j.scitotenv.2015.01.104

1. Introduction

The rapidly-growing world population is projected to reach 9.6 billion by the year 2050 (UN, 2013), a 30% increase with reference to that in 2010s. Moreover, preferences toward meat-based diet and increasing demands for bioenergy crops are also driving an ever-increasing demand for global agricultural production. As a result, FAO (2009) predicted that the global grain production is required to increase by 70% by 2050 to meet these demands. Given the limited additional arable lands and scarce water resources in the world, a significant increase in agricultural fertilizer application is one approach to achieve the required massive increase in global food production. However, in the meanwhile, in order to maintain the current levels of grain production, applications of diverse conventional fertilizers at high rates and for a long period in the agricultural sector have caused serious environmental issues globally. For example, heavy uses of nitrogen (N) and phosphorus (P) fertilizers have become the major anthropogenic factors exacerbating world-wide eutrophication problems in surface freshwater bodies and coastal ecosystems (Conley et al., 2009; Correll, 1998), even affecting people's daily life: A serious algal bloom occurred in Lake Erie in 2014, which forced one of the Ohio's large cities (440,000 in population) to ban use of drinking water for 2 days (Bacon, 2014). In addition, a United States Geological Survey (USGS) report (Dubrovsky and Hamilton, 2010) revealed that 83% of the shallow groundwater under agricultural zones in the US contains nitrates at levels higher than the USEPA regulated maximum contaminant level (MCl) of 10 mg L^{-1} because of intensive uses of N fertilizers and manures. Rosenstock et al. (2014) reported that, due to the increased fertilizer applications in local intensive agriculture, the estimated N loading to the Californian groundwater is 163 kilotonne N yr^{-1} in 2010s, twice higher than the N loading in the 1970s (81 kilotonne N yr^{-1}). Therefore, there is an imperative research need to develop innovative fertilizers to increase crop yields, enhance efficiencies of plant-nutrient uses, and minimize environmental disruptions for global sustainable development.

In the context of sustainable agriculture, applying innovative nanotechnology in agriculture (including fertilizer development) is regarded as one of the promising approaches to significantly increase crop production and feed the world's rapidly-growing population (Lal, 2008). Concerned by the low efficiency (merely 30–50%) of the conventional fertilizers and few management options to enhance the rates, DeRosa et al. (2010) also urged application of nanotechnology to fertilizer research and development. Although several of these agricultural experts have been interested in development and application of nanomaterial-related fertilizers (Ghormade et al., 2011; Khot et al., 2012; Lal, 2008; Nair et al., 2010), the directly-related research is lacking. However, some recent research in nanotechnology has demonstrated the promising perspective of nanofertilizer development and application. For example, observations that C nanotubes (CNTs) and zinc oxide nanoparticles (NPs) can penetrate tomato (*Lycopersicon esculentum*) plant roots or seed tissues indicate that a new nutrient delivery system can be developed through exploiting the nanoscale porous domains on plant surfaces (DeRosa et al., 2010). Thus, the major objective of this review is to collate, analyze, and synthesize the most current knowledge regarding these NPs and nanomaterials (NMs) which can improve plants' growth and yields and/or reduce the environmental risks (such as those caused by N and P applications). These NMs are promising candidates of a new type of fertilizers (nanofertilizers) to meet the incoming challenges of food availability and environmental protection.

1.1. Nanomaterials and nanofertilizers

NMs are defined as materials with a single unit between 1 and 100 nanometers (nm) in size in at least one dimension. Accordingly, nanofertilizers are either NMs which can supply one or more nutrients to the plants and enhance their growth and yields, or those which facilitate to improve the performance of conventional fertilizers, but do not directly provide crops with nutrients. For convenient discussion in this review, the former are collectively called nanofertilizers and the latter nanomaterial-enhanced fertilizers. Furthermore, nanofertilizers could be classified as macronutrient nanofertilizers and micronutrient nanofertilizers. Compared with the conventional ones, nanofertilizers are expected to significantly improve crops' growth and yields; enhance the efficiency of fertilizer use; reduce nutrient losses; and/or minimize the adverse environmental impacts.

1.2. Mechanisms of nanofertilizer uptake by plants

It is possible for NPs to directly enter plant cells through the sieve-like cell wall structures if the particle sizes are smaller than the sizes of cell wall pores (5 to 20 nm). But further proceeding of NPs through cell membrane, interactions with cytoplasm, and utilization of NP-carrying nutrients are too complicated and beyond scope of this review, partly also because of the lack of related research (Nair et al., 2010). However, no research has excluded it as one of the primary mechanisms in this regard that the nutrient elements could be absorbed by plant root system through nanoparticle dissolution in water/soil solution. In other words, NPs simply dissolve in solution and release the nutrient(s) as soluble ions (Eqs. (1)–(3)). Plants absorb the soluble nutrient ions indiscriminately as those from the dissolved conventional fertilizers. But, the dissolution rate and extent of NPs in water/soil solution should be higher than those of the related bulk solids because of the much smaller particle sizes and higher specific surface areas of the former.

$$Ca_5(PO_4)_3OH(NPs) \Leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^- \quad (1)$$

$$ZnO(NPs) + H_2O \Leftrightarrow Zn^{2+} + 2OH^- \quad (2)$$

$$2Cu(NPs) + 2H_2O + O2 \Leftrightarrow 2Cu^{2+} + 4OH^- \quad (3)$$