Geoderma 323 (2018) 116–125

Contents lists available at ScienceDirect

Geoderma

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

Tailoring hydroxyapatite nanoparticles to increase their efficiency as phosphorus fertilisers in soils

Lei Xiong[a], Peng Wang[b,c,*], Peter M. Kopittke[a]

[a] The University of Queensland, School of Agriculture and Food Sciences, St Lucia 4072, Australia
[b] Nanjing Agricultural University, College of Resources and Environmental Sciences, Nanjing 210095, China
[c] The University of Queensland, Centre for Soil and Environmental Research, School of Agriculture and Food Sciences, St Lucia 4072, Australia

ARTICLE INFO

Handling Editor: Yvan Capowiez

Keywords:
Hydroxyapatite
Phosphorus pools
P availability
Release
Nanoparticles

ABSTRACT

Hydroxyapatite nanoparticles (HA-NPs) have been proposed as a novel phosphorus (P) fertiliser that could potentially provide increased efficiency through controlled release. In the present study, three types of HA-NPs were synthesised with differences in surface charge and hydrodynamic sizes before being incubated in two P-deficient soils (an Ultisol and a Vertisol) in the laboratory for up to 240 d. The three types of HA-NPs had surface charge values of +21 (± 4.3), 0 (± 3.5) and −12 (± 2.7) mV in a neutral medium (pH 7). In the Ultisol (pH 4.7), the addition of HA-NPs resulted in a smaller initial increase in P availability than triple superphosphate (TSP) due to their lower solubility. However, P availability in the TSP treatment decreased over time due to adsorption of P to the soil constituents, with a concomitant increase in the NaOH-extractable P fraction. In contrast, the release of P from the HA-NPs remained relatively constant over the entire incubation period. After 45 d, the soils amended with negatively charged HA-NPs had higher levels of available P when estimated using diffusive gradients in thin films (DGT-P) compared to both the neutral and the positively charged HA-NPs. In the Vertisol (pH 8.2), although the addition of TSP increased P availability markedly, amendment with the three HA-NPs did not increase P availability due to the low solubility of hydroxyapatite at this high pH. Indeed, for the Vertisol, most of the P added as HA-NPs remained in the Ca-P fraction. Our results show that for the acidic Ultisol, HA-NPs with altered surface charges are potentially a useful form of slow release P.

1. Introduction

It is estimated that worldwide, a total of 5.7 billion ha of land contains low levels of plant-available P (Cakmak, 2002). As a result, in 2016 alone, an estimated 261 million tons of phosphate rock was mined and used globally for crop production (USGS, 2017), with this predicted to increase further due to an increased population, changing diets, climate change policies, and the silent demand in Africa (Steen, 1998; European Fertiliser Manufacturers Association, 2000; Cordell and White, 2011). However, using currently-available fertiliser technology and agronomic methods, only 10–20% of the P which is applied as fertiliser to soils is actually absorbed by plants (Holford, 1997) with the remaining 80–90% rapidly transformed into forms that are of low availability (Hedley and McLaughlin, 2005). Thus, there is a need to increase the efficiency of P usage. Furthermore, of the 14 nutrients that are essential for plants, global reserves of P are the smallest (Gilbert et al., 2009) with the majority of these in a single country (Morocco). Although there is disagreement, many have estimated that these P reserves are sufficient for only a further 50–125 years (Cordell et al., 2009; Gilbert et al., 2009). As a result, the use of the remaining P reserves must be efficient, with the supply of P fertilisers influenced both by scarcity and political instability.

Application of conventional soluble P fertilisers, such as triple superphosphate (TSP, $Ca[H_2PO_4]_2$), monoammonium phosphate (MAP, $NH_4H_2PO_4$), diammonium phosphate (DAP, $[NH_4]_2HPO_4$), ammonium polyphosphate liquid (APP, $[NH_4PO_3]_n$), results in a rapid increase in the concentration of P in the soil solution, generally exceeding the saturation value of roots for P uptake (Kang et al., 2011). This soluble P remains in the soil solution where it potentially reacts with soil components, including through specific adsorption on the surface of clay minerals and Fe/Al oxides and hydroxides, and precipitation with Fe/Al and Ca minerals (Folle et al., 1995). As a result, several additions of P compounds may be required over time in order to maintain adequate levels of P to meet plant nutrition. Conversely, this over-application of P fertilisers may also result in adverse environmental outcomes through their movement into water bodies, which results in eutrophication.

In order to meet the nutritional requirements of the plant while also increasing the efficiency of uptake (i.e. decreasing the reaction of P

---

* Corresponding author at: Nanjing Agricultural University, College of Resources and Environmental Sciences, Nanjing 210095, China.
E-mail address: p.wang3@njau.edu.cn (P. Wang).

https://doi.org/10.1016/j.geoderma.2018.03.002
Received 30 November 2017; Received in revised form 2 March 2018; Accepted 3 March 2018

within soils) and decreasing adverse environmental outcomes, it is useful to consider slow-release forms of P. Nanoparticle-based fertilisers, defined as particle having at least one dimension between molecular and micrometre scales, have been proposed as a novel technology to enhance nutrient-use efficiency and reduce environmental risks (Liu and Lal, 2014). Ideally, the nutrients from nanofertilisers should be released in a controlled manner that corresponds approximately to plant demands. Where it is possible to match nutrient release to the demands of the plant, this not only limits the conversion of the nutrient (P) to chemical forms that are of reduced availability to plants, but also reduces loss to other environmental compartments (DeRosa et al., 2010; Wang et al., 2016). Concomitantly, by increasing the efficiency with which the applied nutrients are utilised, this will also decrease the frequency with which the fertilisers need to be applied. Although nanofertilisers have been demonstrated to be potentially promising (Ghormade et al., 2011; Khot et al., 2012), comparatively little information is available in the literature. Recently hydroxyapatite nanoparticles (HA-NPs) have been examined to determine if they are suitable as an alternative to conventional P fertilisers. Liu and Lal (2014) examined carboxymethyl cellulose (CMC) stabilized HA-NPs on soybean (*Glycine* max) in an inert growing medium (50% perlite and 50% peat moss) utilising a pot experiment. The data showed that the application of HA-NPs increased growth rate by 32.6% and seed yield by 20.4% compared to those with TSP. Specifically, these authors found that below-ground biomass increased by 41.2% while above-ground biomass increased by 18% compared to TSP. Similarly, Montalvo et al. (2015) evaluated the efficiency of HA-NPs in two acid and strongly P-sorbing soils, an Andisol and an Oxisol. For these two soils, Montalvo et al. (2015) found that although HA-NPs were more effective than bulk hydroxyapatite (Bulk HAP) (presumably due to their smaller particle size), TSP was still the most efficient fertiliser. Thus, these studies demonstrate the need for further work to examine the suitability of HA-NPs, particularly as influenced by soil properties. Also of interest is how the modification of the properties of HA-NPs influences their behaviour in soils. For example, modification of the surface charge of nanoparticles would potentially alter how they interact with the charged soil colloids.

The aim of the present study was to examine the suitability of HA-NPs as P fertilisers. Of particular interest, we examined HA-NPs that differed in their surface charge, with this expected to not only alter how the NPs interact with the soil solid phase, but also influence their self-aggregation when applied to soil. Accordingly, we prepared three forms of HA-NPs with negative, neutral, or positive surface charges. Using these three forms of HA-NPs plus TSP and Bulk HAP, we first compared solubility of these HA-NPs to Bulk HAP as well as examining the influence of pH on surface properties of the NPs. Secondly, a laboratory incubation study was conducted using two P-deficient soils (an acidic Ultisol and an alkaline Vertisol) that differed widely in their properties. Using the two soils, we examined whether the surface properties (specifically, the surface charge) of the HA-NPs influences their interaction with the soil. Soils were incubated for up to 240 d, with changes in P forms and availability examined. Thirdly, the effect of soil pH on P availability of HA-NPs was examined by incubating soils amended with HA-NPs after adjusting the pH of the soil to different values. It is hoped that the information obtained in the present study will assist in the development of a strategy that maximises P fertiliser use efficiency in order to supply P according to the nutritional demands of plants.

2. Material and methods

2.1. Synthesis and surface modification of HA-NPs

The HA-NPs were synthesised by wet chemical deposition according to the methods described by Lee et al. (2006). Briefly, a 0.6 M $Ca(NO_3)_2$ solution was prepared by dissolving 14.2 g $Ca(NO_3)_2 \cdot 4H_2O$ in 50 mL deionized (DI) water, with pH adjusted to 10 using aqueous $NH_3 \cdot H_2O$ (28–30%) and DI water used to increase the volume to 100 mL. A 0.36 M $(NH_4)_2HPO_4$ solution was prepared by dissolving 4.76 g $(NH_4)_2HPO_4$ in 50 mL DI water, with pH adjusted to 9 using aqueous $NH_3 \cdot H_2O$ and DI water used to increase the volume to 100 mL. The 100 mL $(NH_4)_2HPO_4$ solution was added dropwise to the 100 mL of the $Ca(NO_3)_2$ solution with continuous stirring. This resulted in the formation of a white precipitate, with pH maintained above 9 using aqueous $NH_3 \cdot H_2O$. The reaction mixture was aged in a round-bottom flask while stirring for 20 h at 80 °C, after which a colloidal dispersion of nanoparticles was obtained. The mixture was centrifuged and the precipitate washed three times using DI water.

We prepared three types of HA-NPs differing in their surface charge. Glycine and ammonium citrate dibasic were used for surface modification to obtain HA-NPs with either a positive surface charge or a negative surface charge, plus a control (uncharged) (Li et al., 2011; Lee et al., 2013). Briefly, a 1.2 M modifier solution was prepared by dissolving 9 g of glycine or 27 g of ammonium citrate dibasic in 100 mL DI water. The modifier solution was added to the 0.6 M $Ca(NO_3)_2$ solution before the $(NH_4)_2HPO_4$ solution was added and the precipitate was formed. The reaction mixture was aged in a round-bottom flask while stirring for 20 h at 80 °C, after which a colloidal dispersion of nanoparticles was obtained. The mixture was centrifuged and the precipitate washed three times using DI water.

2.2. Characterisation of synthesised HA-NPs

Synthesised HA-NPs colloids were dried at 40 °C for 48 h and then ground to < 1 mm prior to analysis (Knowles et al., 2000). Particle morphology was examined using scanning electron microscopy (SEM). A single drop of the HA-NPs suspension (100 mg/L) was placed on a sample holder and dried at 40 °C for 12 h before being coated with iridium three times (ca. 8 nm per coating) and plasma cleaned. Images were captured using SEM (JEOL JSM-7100F, Japan) at an acceleration voltage of 20 kV. Mineral phase identification was conducted by X-ray diffraction (XRD). Measurements were performed using a Bruker D8-Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany), operating in the reflection mode with Cu-Kα radiation ($\lambda = 1.54$ Å) at 40 kV, 10–70° 2-theta. Functional groups were examined using Fourier transform infrared spectrometer (FTIR, Nicolet Spectrometer, Madison, USA). Next, we examined the average hydrodynamic diameter (HD) and the zeta potential (Keller et al., 2010) using dynamic light scattering (DLS, Zetasizer Nano ZS Malvern Instruments, Worcestershire, UK). Approximately 100 mg/L of synthesised HA-NPs solution was dispersed using ultrasound irradiation (750 W, Vibra Cell VCX 750) for 20 min before measurement for DH and zeta potential. To determine the effect of pH on DH and zeta potential, additional samples were adjusted to pH values between 5 and 11 using KOH or HCl.

The solubility of HA-NPs (and the associated K_{sp} values) was determined by measuring the concentration of soluble P and Ca in a suspension (1000 mg/L). Specifically, the suspension was dispersed using ultrasound irradiation (750 W) for 20 min before being filtered using a centrifuge filter unit (with a cut-off of 1–2 nm) by centrifugation. The filtrate was transferred to a 10 mL tube, with 0.3 mL of HNO_3 (70%) added, and the concentration of Ca was analysed using inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista Pro), whereas the concentration of P was determined using Flow Injection Analyser (FIA, Lachat QuikChem8500, Hach Company, USA). The molar ratio of total Ca:P of the solid HA-NPs was determined by measuring the concentration of Ca and P by ICP-OES after dissolution of the solid matrix by adding concentrated HNO_3 (70%).

2.3. Soil collection and characterisation

We collected topsoil (0–20 cm) from two P-deficient soils (an Ultisol and a Vertisol, Soil Survey Staff (2014)) that differed in many of their properties (Table 1). The Ultisol was collected from a forested area in