



Reduction of orthophosphates loss in agricultural soil by nano calcium sulfate



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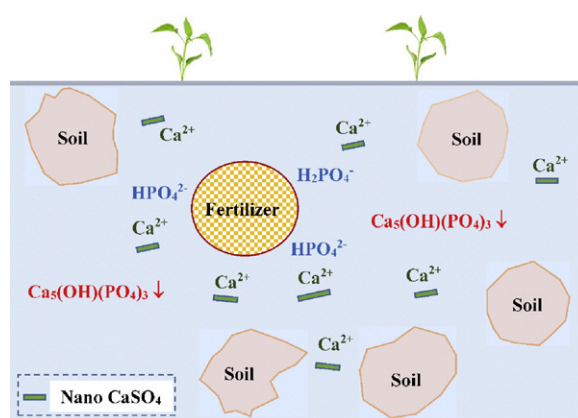
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HIGHLIGHTS

- We studied calcium sulfate to reduce orthophosphates loss from agriculture soil.
- Calcium sulfate reduced water extractable phosphorus (WEP).
- Nano calcium sulfate further reduced WEP because of great specific surface area.
- Calcium hydroxyapatite has the lowest solubility in the Ca and P precipitates.

GRAPHICAL ABSTRACT



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ABSTRACT

Nutrient loss from soil, especially phosphorous (P) from farmlands to natural water bodies via surface runoff or infiltration, have caused significant eutrophication problems. This is because dissolved orthophosphates are usually the limiting nutrient for algal blooms. Currently, available techniques to control eutrophication are surprisingly scarce. Calcium sulfate or gypsum is a common soil amendment and has a strong complexation to orthophosphates. The results showed that calcium sulfate reduced the amount of water extractable P (WEP) through soil incubation tests, suggesting less P loss from farmlands. A greater decrease in WEP occurred with a greater dosage of calcium sulfate. Compared to conventional coarse calcium sulfate, nano calcium sulfate further reduced WEP by providing a much greater specific surface area, higher solubility, better contact with the fertilizer and the soil particles, and superior dispersibility. The enhancement of the nano calcium sulfate for WEP reduction is more apparent for a pellet- than a powdered- fertilizer. At the dosage of Ca/P weight ratio of 2.8, the WEP decreased by $31 \pm 5\%$ with the nano calcium sulfate compared to $20 \pm 5\%$ decrease with the coarse calcium sulfate when the pellet fertilizer was used. Computation of the chemical equilibrium speciation shows that calcium

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Nano calcium sulfate
Gypsum

hydroxyapatite has the lowest solubility. However, other mineral phases such as hydroxycalcium phosphate, dicalcium phosphate dihydrate, octacalcium phosphate, and tricalcium phosphate might form preceding to calcium hydroxyapatite. Since calcium sulfate is the major product of the flue gas desulfurization (FGD) process, this study demonstrates a potential beneficial reuse and reduction of the solid FGD waste.

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1. Introduction

Agriculture is of critical importance to the economy and people's life in the world. However, fertilizers used in farming have brought significant threats to the aquatic environment. More specifically, surface runoff and infiltration loaded with significant amounts of nitrogen (N) and P have been causing water body eutrophication, which is demonstrated by the overgrowth of algae. Eutrophication brings a series of adverse ecological and water quality problems such as fish deaths, shifts in species composition, blooms of harmful algae, hypoxia in water body, as well as toxins, taste and odor in drinking water (Lowe et al., 2008). For example, in August 2014, a toxic algal bloom in Lake Erie caused the tap water to be unsafe to drink for 400,000 residents living in Toledo, Ohio, USA for three days (Morrone and McKee, 2015). In the Upper Wabash River basin, which drains 18,655 km² of central Indiana and parts of western Ohio, USA, the dominant land use is agriculture (92%) (Hoggatt, 1975). Based on the data in 2003, 30% of 111 samples from the Upper Wabash River were above eutrophic level (Lowe et al., 2008). Consequently, it is of great importance to prevent natural water bodies from eutrophication in order to protect the water quality, the ecosystem and the public health and welfare.

P, especially in soluble form is usually the limiting nutrient for algae growth (Eaton and Franson, 2005), because the exchange of N between the atmosphere and a water body and fixation of atmospheric N by some blue-green algae can be sufficient to prevent N from limiting biological productivity (Sharpley et al., 1987). The physiological processes of algae growth are balanced when the cellular carbon, N and P atomic ratio is 106:16:1 (Borchardt, 1996, Redfield, 1958). The critical soluble P concentration is 10 µg/L (Sawyer, 1947), which if exceeded may accelerate the eutrophication of water. Phosphorus in natural waters occurs almost solely as phosphates (Eaton and Franson, 2005). Phosphates are classified as orthophosphates (PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, H₃PO₄), condensed phosphates (pyro-, meta- and other polyphosphates), and organically bound phosphates (Eaton and Franson, 2005, Elliott, 2013). Of these forms of phosphates, only soluble orthophosphate can be directly utilized by algae (Tchobanoglous et al., 2003). Condensed and organic phosphates must undergo slow hydrolysis through abiotic and/or biotic reactions and convert to orthophosphates before being utilized by algae (Holtan et al., 1988).

Although considerable progress has been made in understanding eutrophication, effective control techniques are surprisingly scarce. The conventional methods to reduce nutrient loss from soils are improved farming practices (e.g., reduce tillage, avoid overdose, and sub-surface injection). Soil testing can determine the background nutrient levels and thus avoid overdose. However, new evidences of water body eutrophication suggest these strategies are not enough. In inorganic fertilizers, P is mainly in the form of orthophosphates (Smil, 2000). An ideal situation is to retain P in the farmlands while reducing soluble P loss via surface runoff or infiltration. More specifically, calcium sulfate including gypsum (CaSO₄·2H₂O), with a strong potential to complex with orthophosphates (Bastin et al., 1999, Felton et al., 2004, Kordlaghari and Rowell, 2006, Pietola, 2008), may be applied to the farmlands. Ca²⁺ from calcium sulfate can not only precipitate or adsorb soluble P in soil pore water, but can also improve soil structural properties like aggregate stability of clay soil for erosion control (Pietola, 2008). For organic- and condensed- phosphates, Ca²⁺ from calcium sulfate may capture and complex with the slowly released orthophosphates from hydrolysis of condensed and/or organic phosphates in

soil. The precipitates of calcium phosphates are more likely to stay in the soil. In addition, since sulfur is required in the synthesis of proteins, sulfate can provide this essential micronutrient for agricultural plants to synthesize sulfhydryl (SH) groups in proteins (Tortora et al., 2010). As a result, calcium sulfate can be a "green" chemical benefiting both agricultural plants and environmental protection.

The efficiency of using calcium sulfate to reduce P in surface runoff or infiltration and precipitate phosphate in water have been reported by several studies. In the study of Felton et al. (2004), gypsum was used to control soluble P from poultry. 98% removal of P was achieved with the 1:1 mass mixing ratio between poultry and gypsum. Pietola (2008) showed that gypsum significantly decreased the loss of P from both inorganic and manure fertilizers and reduced soil erosion. Consistently, Kordlaghari and Rowell (2006) indicated that gypsum significantly increased the sorption of P in soil by forming calcium phosphate. Bastin et al. (1999) reported about 5 mg/L soluble P was removed by 1 g/L of the mixture of iron oxide and gypsum. However, in these studies the efficiency was restricted by the limited specific surface area of calcium sulfate particles. To our best knowledge, there is few study about the effect of nano calcium sulfate to retain P in soil. Nano calcium sulfate has the advantages of a much greater specific surface area, higher solubility (Junyaprasert and Morakul, 2015), better contact with the fertilizers and soil, superior dispersibility and dose-saving capability than conventional calcium sulfate particles. These advantages were expected to enhance the complexations (including precipitation and adsorption) between orthophosphates and Ca, and thus to reduce P loss from farmlands. The main objectives of this study were to i) synthesize nano calcium sulfate; ii) examine the efficiency of nano calcium sulfate to retain orthophosphates in soil; and iii) elucidate the mechanisms of orthophosphates retention by nano calcium sulfate. Water extractable P (WEP) directly relates to the potential P loss via surface runoff or infiltration (Felton et al., 2004, Leytem et al., 2004). The levels of WEP were investigated in this study through soil incubation tests. The efficiency was compared among nano, coarse calcium sulfate and blank soil samples. Since calcium sulfate is the major product of the flue gas desulfurization (FGD) process in coal-fired power plants, this study demonstrates a potential beneficial reuse and reduction of the solid FGD waste.

2. Methodology and materials

2.1. Synthesis of nano calcium sulfate

All chemical reagents were of certified grade. All solutions in this study were prepared with DI water (R = 18.2 MΩ·cm). Nanoparticles of calcium sulfate were prepared in the laboratory by the chemical co-precipitation method (Sawant and Niranjane, 2006) through dissolving 2.466 g of calcium chloride and 0.954 g of sodium dodecyl sulfate in 45 mL DI water. The precipitate was then dissolved in 163.8 mL of ethylene glycol before slowly adding 11.3 mL of concentrated sulfuric acid. Next, 79.8 mL of ethanol was added very slowly to the solution with constant stirring to form a solution containing nano CaSO₄ particles, which were harvested by centrifuge at 3000 rpm for 30 min and purified by rinsing with ethanol several times. Finally, before soil incubation tests, a fresh suspension of nano calcium sulfate particles was produced by rinsing with DI water and centrifuged at 3000 rpm for 15 min four times to remove residual ethanol. The nano calcium sulfate suspension

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