Soil & Tillage Research 180 (2018) 48–62

Contents lists available at ScienceDirect

Soil & Tillage Research

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

Polymer coated novel controlled release rock phosphate formulations for improving phosphorus use efficiency by wheat in an Inceptisol

Abhijit Sarkar[a,b], Dipak Ranjan Biswas[a,*], Samar Chandra Datta[a], Trisha Roy[a,c], Pravash Chandra Moharana[a,d], Siddhartha Sankar Biswas[a], Avijit Ghosh[a]

[a] Division of Soil Science and Agricultural Chemistry, ICAR-Indian Agricultural Research Institute, New Delhi, 110 012, India
[b] ICAR-Indian Institute of Water Management, Bhubaneswar, Odisha, 751 023, India
[c] ICAR-Indian Institute of Soil and Water Conservation, Dehradun, Uttarakhand, 248 195, India
[d] NBSS & LUP, Regional Centre, University Campus, Bhora Ganeshji Road, Udaipur, Rajasthan, 313 001, India

ARTICLE INFO

Keywords:
Controlled release fertilizer
Rock phosphate
Coating agent
Phosphorus use efficiency
Wheat

ABSTRACT

Non-renewable nature of rock phosphate (RP) reserves coupled with low use efficiency of applied phosphorus (P) fertilizers in the soil system results in irreversible loss of huge quantity of P to the environment. The technology of controlled release fertilizers which harmonizes crop demand and release of P from fertilizers are promising to prevent the loss as well as improve the P use efficiency. This article aimed to synthesize and assess some polymer coated novel controlled release rock phosphate formulations to synchronize P release with crop demand and increasing P recovery by wheat. Polymer coated novel products were synthesized by partially acidulating RP with sulphuric and phosphoric acids followed by coating with polyvinyl alcohol and liquid paraffin @ 2 and 3% levels of coating. These products were characterized through X-ray diffraction, fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Phosphorus release pattern from novel coated fertilizers were monitored under controlled conditions in a laboratory incubation experiment at different moisture and temperature regimes. The products were also evaluated for their P supplying capacity to wheat in a greenhouse experiment. Results emanated from incubation study in a P-deficient Typic Haplustept revealed higher release of P at 20% moisture regime and 30 °C temperature. Phosphoric acid based coated products produced greater biomass yield than commercial diammonium phosphate and sulphuric acid formulated products. Product coated with polyvinyl alcohol @ 2% coating released P gradually that synchronized well with the plant P demand and resulted in greater biomass yield, P uptake and recovery by wheat than that of liquid paraffin and 3% level of coating. It can be concluded that novel technology of controlled release RP formulations using different coating agents could be exploited commercially as the alternative to water soluble P-fertilizers for enhancing P use efficiency.

1. Introduction

The fixation of phosphorus (P) as iron (Fe) and aluminium (Al) phosphates in acid soils and calcium (Ca) phosphates in alkaline soils is defined as a historical problem of soil science (Sanders et al., 2012). This historical problem corresponds to very low P use efficiency (PUE) of applied P-fertilizer in the soil system even after employing the best management practices for crop production. Out of the total P extracted from earth crust for the provision of food, only 15% is consumed by the human food chain and the rest is lost to the environment (Suh and Lee, 2011). Along with low PUE, the deficiency of P in soils across the globe is also wide-spread with 43% of the world soils being P-deficient (Liu et al., 2012). Farmers around the world depends on chemical P-fertilizers to correct the P-deficiency and sustain the agricultural production system. However, the complex chemistry of P along with its low PUE inspires the farmers to apply huge quantity of P-fertilizers causing ecological imbalance, pollution and also incurs huge cost. The biogeochemical movement of P is uni-directional with the P mined from the reserves moving to distant location for various purposes like agriculture, processing, manufacturing *etc*. which makes the recycling of P more difficult, with major share being unused and lost outside the system (Schröder et al., 2011).

All the P-fertilizers applied to soil system is derived from rock phosphates (RP) which is a finite, non-renewable natural resource with an estimated life-span of 105–470 years (Prud'homme, 2006). Current levels of food production is not possible without this finite storage and

* Corresponding author.
E-mail addresses: drb_ssac@yahoo.com, drb_ssac@iari.res.in (D.R. Biswas).

https://doi.org/10.1016/j.still.2018.02.009
Received 16 September 2017; Received in revised form 22 January 2018; Accepted 20 February 2018
0167-1987/

considering long-term food security it is imperative that the use of RP in sustainable and equitable manner is not only intra-generation matter but also an inter-generational perspective (Edixhoven et al., 2014). Several recent papers deal with concerns about the longevity of the supply of the mineral phosphate (Scholz and Wellmer et al., 2016). The finite nature of the RP reserves along with the low use efficiency have triggered many research to improve the PUE from different P sources along with exploiting the low-grade P reserves (< 20% P_2O_5) of poor economic viability to find some alternative source to the costly P-fertilizers. Some of the commonly used technologies are partial acidulation of rock phosphates (Biswas and Narayanasamy, 1995), preparation of RP enriched compost (Biswas and Narayanasamy, 2006), use of P-solubilizing microorganisms (Biswas and Narayanasamy, 2002; Vassilev et al., 2006) which have been tried and tested. The recent advancements in P-fertilizers involves coating of soluble P sources with hydrophobic or partially hydro-phillic compounds (Hanafi et al., 2002) or mixture with superabsorbents (Bortolin et al., 2012) or nano sized clay particles (Basak et al., 2012, Tang et al., 2017) or RP mixed with organic acid loaded nanoclay polymer composites (Roy et al., 2015, 2018; Giroto et al., 2017). These technologies have proved to be promising alternative sources to the costly P-fertilizers as well as improved the PUE but have not yet been adopted at large scale. Besides these, the recent development in smart fertilizer delivery systems or the new generation fertilizers is a good alternative to commercially available P-fertilizers to improve the use efficiency and enhance resource utilization (Fernandes da Cruz et al., 2017; Marcela et al., 2018).

The control release fertilizer (CRF) is one such new generation fertilizer which is designd to release plant nutrients in a steady manner so as to synchronize the release with crop demand (Shaviv, 2001). This technology not only helps in improving the nutrient use efficiency but also suggests a suitable mechanism to reduce environmental hazards posed by indiscriminate and execessive use of fertilizers (Shaviv and Mikkelsen, 1993; Shaviv, 1999). In general, control release fertilizers exhibit numerous preferences over the traditional water soluble fertilizers, for example, savings in huge quantities of fertilizers, reducing the rate of release of fertilizer nutrients and thus supplying nutrients to crops for longer period of growth, and increase use efficiency of the fertilizer (Davidson and Gu, 2012). Additionally, they improve germination rates, reduces the salt concentration due to fertilizer and thereby seed toxicity, inhibits nutrient losses, hazardous emissions, leaf burning and improves overall soil health (Zhan et al., 2004).

In the recent past, there is renewed interest to establish this concept for developing new controlled release P products. One of the possible means of applications of controlled release fertilizers is to apply them in association with super-absorbent which is able to release their nutrient in a controlled manner (Li et al., 2005). Also, various coating agents can be employed to regulate the nutrient release. Polymer coating of monoammonium phosphate (MAP) granules increased the fertilizer PUE up to 32.6% along with increasing the crop yield (Malhi et al., 2002). However, very limited information is available on the development of controlled release P-fertilizers using low-grade RP acidulated with mineral acids followed by coating with suitable coating agents. In this study, we investigated the controlled release properties of coated low-grade RP acidulated products in laboratory and pot experiments against conventional water soluble P-fertilizers like diammonium phosphate (DAP). The objectives were to (i) develop and characterize novel coated controlled release rock phosphate formulations (CRRPFs) by treating low-grade RP from Udaipur (India) deposits with mineral acids (H_2SO_4 and H_3PO_4) followed by coating with polyvinyl alcohol and liquid paraffin; (ii) to check their performances as controlled released P-fertilizer as evident from their P release pattern under laboratory conditions; and (iii) to evaluate their effectiveness as P-fertilizer in an Inceptisol using wheat (*Triticum aestivum* L.) as the test crop.

2. Materials and methods

2.1. Rock phosphate

Rock phosphate (RP) was obtained from the deposits of Rajasthan State Mines and Minerals Limited, Udaipur, Rajasthan, India. The ground RP had a particle size of 100 mesh. It is having 7.64 ± 0.78% total P, 6.53% total Ca, 5.61% total Mg, and 1000, 665, 22.8 and 43.1 $mg\,kg^{-1}$ of total Fe, Mn, Cu and Zn, respectively. The heavy metal concentrations of Cd, Pb and Ni were 0.52, 6.01 and 17.8 $mg\,kg^{-1}$, respectively. On the basis of P content, this rock phosphate can be classified as low-grade rock phosphate.

2.2. Acids

The laboratory grade H_2SO_4 (98% concentrated, v/v) having sp. gr. 1.84 $g\,cm^{-3}$ and H_3PO_4 (76% concentrated, v/v) having sp. gr. 1.75 $g\,cm^{-3}$ were used in this study for acidulation of the RP.

2.3. Coating agents

Two coating agents namely, polyvinyl alcohol (a hydrophilic polymer) and liquid paraffin (a hydrophobic polymer) were used @ 2 and 3% (w/w) levels. Coating agents were selected based on their hydrophobicity. It is reported that polyvinyl alcohol has surface pendant OH^- group which may form H-bond with water molecule and form water hull. It also acts as a weak hydrogel after absorbing or reacting with water. It may also be deprotonated (H^+) and form anionic ligand, which also increase the P release from native soil (Reis et al., 2006). Liquid paraffin is a mixture of hydrocarbon derived from petroleum product. It has long C—H bond (hydrophobic) which does not form any bond with water and generally repel the water molecule.

2.4. Synthesis of controlled release RP formulations

For synthesis of coated CRRPFs, ground RP (500 g each) was placed in two separate reaction vessels. It is hypothesized that for complete acidulation to prepare single superphosphate (SSP) about 60 kg of H_2SO_4 is required to react with 100 kg RP containing 30% P_2O_5 (Biswas and Narayanasamy, 1995, 1998). Considering this as the basis, the amount of H_2SO_4 and RP were calculated, while the amount of H_3PO_4 was calculated on the basis of equivalent acidity of H_2SO_4. Based on this, the required amounts of H_2SO_4 (94.5 mL) and H_3PO_4 (75 mL) were added to respective vessels drop by drop along with continuous mechanical stirring, which resulted in two different RP-formulations namely, RP + H_2SO_4 (Eq. (1)) and RP + H_3PO_4 (Eq. (2)), respectively.

$$Ca_{10}(PO_4)_6F_2 + H_2SO_4 + H_2O \rightarrow Ca(H_2PO_4)_2{\cdot}H_2O + CaSO_4{\cdot}2H_2O + HF \quad (1)$$

$$Ca_{10}(PO_4)_6F_2 + H_3PO_4 + H_2O \rightarrow Ca(H_2PO_4)_2{\cdot}H_2O + HF \quad (2)$$

The materials were allowed to complete the reaction for 10–15 min and then left for drying for 4–6 h under ambient condition (25 ± 1 °C). After drying, RP + H_2SO_4 and RP + H_3PO_4 formulations were ground and sieved through a 2-mm nylon sieve to get homogeneous and granular form of the products. The RP-acid formulations were then coated with PVA and LP at two levels of coating (2 and 3%, w/w). The coated materials were finally kept in vacuum desiccator for drying for 24 h and subsequently used as coated controlled release rock phosphate formulations (CRRPFs) for further use.

2.5. Characterizations of coated CRRPFs

2.5.1. Chemical characterization of coated CRRPFs

Chemical characterization of the novel fertilizer materials were done and results are presented in Table 1. Free acidity – of the coated