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Natural oil and clay-based fertilizer products for slow release of phosphorus in sodic soil

ATHULYA S., MANDIRA BARMAN AND V.K. SHARMA

Division of Soil Science and Agricultural Chemistry, ICAR-Indian Agricultural Research Institute, New Delhi 110 012, India

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ABSTRACT

Controlled nutrient release is one of the most effective fertilizer management strategies for increasing nutrient recovery efficiency while conserving resources and reducing environmental pollution. Nine slow release phosphatic fertilizer products were prepared using various combinations of naturally polymerizing oil (NPO), clay and commercial di-ammonium phosphate (DAP). An incubation study was conducted for 60 days in medium phosphorus (P) containing sodic soil to evaluate the efficacy of synthesized products as controlled release fertilizers (CRFs). Non-destructive sampling was followed and the P released in the soil samples was extracted using 0.01 M $CaCl_2$. The uncoated DAP released almost 60% (4.2g P released per kg of soil out of 7.6 g P added per kg of soil) of the applied P by the end of incubation period; whereas, the release of P from oil-coated DAPs (OC-DAPs) ranges from 4-11% throughout the study period and were significantly less from uncoated DAP by a huge margin. Out of various combinations of OC-DAPs, those formulations with highest NPO and clay tend to have the lowest P release. Because of the sustained and controlled release of P from OC-DAPs, these products can be used as slow or controlled-release fertilizers because they supply nutrients for a longer period of time and thereby enhance nutrient use efficiency. Hence, these oil and clay coated DAP products could be an alternative option to produce cost-effective P fertilizers.

Keywords: Controlled release fertilizer, Naturally polymerizing oil, Clay, Di-ammonium phosphate

INTRODUCTON

Phosphorus (P) is widely known as the ‘key of life’ as it is intimately associated with all life processes and is a vital constituent of every living cell. An ample quantity of P is required to achieve optimum crop yield (Frossard *et al.,* 2000). Despite being the eleventh most abundant element in earth's crust, P is a substantially deficient nutrient element in majority of arable soils worldwide due to its complex chemistry. The tendency of P to form insoluble chemical compounds with soil constituents renders it unavailable to plants and thereby makes only 0.1% of the total P in soil available for uptake by plants (Roy *et al.,* 2018). Most widely used phosphatic fertilizers in our country are di-ammonium phosphate (DAP) and single super phosphate (SSP) which are water soluble and has an extremely low phosphorus use efficiency (PUE) ranging from 15-20%(Carpenter, 2005). Such P fertilizers demands its application in huge quantities to soil to meet the plant requirement. This indiscriminate use of phosphatic fertilizers leads to depletion of the world’s reserves of their non-renewable deposits (Mouat*et al.,* 2023). Hence, measures must be taken to tackle the above-mentioned drawbacks of water-soluble P fertilizers. Scientists need to come up with fertilizer products which have higher PUE, are eco-friendly, and can supply P in a slow and controlled manner to plants (Sanyal *et al.,* 2015). In this regard, controlled release fertilizers (CRFs) are the best products to enhance nutrient recovery efficiencies. The fertilizers known as CRFs have a propensity for delayed, regulated nutrient delivery that may synchronize with plant nutrient requirements (Trenkel *et al.,* 2021).

Hence, in order to obtain delayed and controlled release of nutrients from the water-soluble fertilizer granules, scientists have come up with coating technique to increase fertilizers' efficiency, improve stability and lessen their adverse effects on environment. A number of researchers created CRFs by adding nutrients to hydrogel polymer matrix, covering the surface of commercial fertilizers, and adding nano-fractions of unusual resources among which surface coating is the most well-liked and practical method from an economic standpoint (Sarkar *et*

Corresponding author email: mandira.ssaciari@gmail.com, Senior Scientist, Division of Soil Science and Agricultural chemistry, ICAR-IARI, New Delhi

al, 2017). In fact, numerous studies have looked at synthetic polymers including polyethylene, poly acrylic acid-co-acrylamide, polybutyl methacrylate and polystyrene as hydrophobic coating materials of fertilizers. These coating materials, however, are not biodegradable and their toxicity also has cast doubt on the long-term viability of such an option. As a result, further research projects focused on use of polysaccharides such as cellulose and chitosan as biodegradable coating materials for granular fertilizers. (Mandal *et al.,* 2015). However, because of their very hydrophilic nature, poor mechanical qualities and insolubility in organic solvents, the application of these polysaccharides as coating materials has not produced the desired results. In light of the foregoing conclusions, researchers have recently concentrated their study on coatings made of hydrophobic biopolymers, such as aliphatic polyesters (Neto *et al*, 2023). Although this new approach has led to the development of innovative coating materials characterized by their biodegradability and hydrophobic character, the cost and marketability of the coating materials based on aliphatic polyesters remain a constraint so far. In this regard, naturally polymerizing oil (NPO) holds great importance as it is readily available, inexpensive, contains a higher proportion of polyunsaturated fatty acids than monounsaturated fatty acids (Svane*et al.,* 2006). Although NPOs are considered faster drying than majority of other natural oils, it may take some time to get completely dried. In this regard, few works have been directed toward developing coatings for fertilizers using clays, organic polymers, chitosan-montmorillonite composites and paraffin wax (Xiaoyue*t al.,* 2013 and Assimi *et al.,* 2020). Unfortunately, knowledge on oil and clay-based formulations for controlled release fertilizer preparation and the evaluation of same in various Indian soils is extremely limited. In light of the aforementioned literature, new controlled-release phosphatic fertilizers were formulated using NPO, commercial DAP, and clay and a research study was conducted to evaluate the efficacy of NPO and clay-based formulation in releasing P in a medium P containing sodic soil of Karnal, Haryana.

MATERIALS AND METHODS

Soil sample collection and analysis

Soil sample with medium P content was collected from Karnal, Haryana(29° 43’ N latitude and 76° 58’ E longitude). It has an elevation of 245 m above mean sea level, with average annual rainfall ranging from 750–1171 mm. Average annual temperature ranges from 4 to 40°C. The soil belongs to the order Aridisol. Collected soil sample was analysed for physical and chemical properties using standard protocols. The hydrometer method was used to determine the mechanical composition of soil, i.e., the proportion of sand, silt, and clay particles (Bouyoucos, 1962). The texture of the soil was determined using the textural triangle proposed by USDA (Gee *et al.,* 1986). The pH of soil sample was determined in a 1:2 (soil:water) suspension using a digital pH meter with combined electrode (glass and calomel electrodes). The electrical conductivity (EC) was measured in the supernatant liquid of the same extract using a conductivity meter and expressed in dSm^{-1} at 25°C. The organic carbon content of soil was estimated using the Walkley and Black wet oxidation method(1934). The cation exchange capacity (CEC) was evaluated using the ammonium acetate method proposed by Jackson (1973). Available nitrogen in the soil sample was estimated using alkaline $KMnO_4$ method given by Subbiah and Asija (1956). In order to estimate phosphorus (P) content of soil sample, P was extracted using Olsen’s reagent (Olsen, 1954) and was estimated using ascorbic acid blue colour method (Watanabe and Olsen, 1965). Available potassium (K) and sodium (Na) were determined by extracting the soil sample with 1*N* ammonium acetate (pH 7.0) and Na and K content in the extracts were measured by flame photometer. Soil samples were extracted with 0.005 *M* DTPA, 0.01 *M* $CaCl_2$ and 0.1M TEA (Lindsay and Norvell, 1978) to determine micronutrients. Available zinc (Zn), copper (Cu), iron (Fe) and manganese (Mn) in the extracts were determined by flame atomic absorption spectrophotometer (AAS).

Experimental set up

In a laboratory incubation experiment, naturally polymerizing oil (NPO) and clay coated di-ammonium phosphate (DAP) fertilizer products were evaluated for their P release property using a sodic soil. The fertilizer products were prepared using various combinations of NPO, clay and DAP fertilizer. Overall, nine formulations were prepared by varying the amount of NPO and clay (Table 1). A 200 g soil was taken in plastic bottles and a uniform dose of P (7.61g Pkg^{-1}soil) was added in all the bottles containing soil samples through various oil-coated fertilizer products (OC-DAP) and commercial DAP. Moisture content of the samples was maintained at field capacity and the experiment was set up at 25ºC. Release of P from OC-DAP, DAP and control samples were measured at 7,15,30, 45 and 60 days in non-destructive manner. Phosphorus was extracted from the incubated samples using 0.01 M $CaCl_2$and was estimated using ascorbic acid blue colour method at 720 nm using UV-VIS Spectrophotometer (Jackson,1973).

Table 1: Various combinations of NPO, clay and commercial DAP

Product	Combination
OC- DAP_1	100 g Commercial DAP+ 5 mL NPO
OC- DAP_2	100 g Commercial DAP+ 5 mL NPO + 2.5 g clay
OC- DAP_3	100 g Commercial DAP+ 5 mL NPO + 5 g clay
OC- DAP_4	100 g Commercial DAP+7.5 mL
OC- DAP_5	100 g Commercial DAP+ 7.5 mL NPO + 2.5 g clay
OC- DAP_6	100 g Commercial DAP+7.5 mL NPO+ 5 g clay
OC- DAP_7	100 g Commercial DAP+10 mL NPO
OC- DAP_8	100 g Commercial DAP+ 10 mL NPO+ 2.5 g clay
OC- DAP_9	100 g Commercial DAP+10 mL NPO+ 5 g clay

OC-DAP- Oil coated DAP, NPO- Naturally polymerizing oil, DAP- Di-ammonium phosphate

Statistical Analysis

The data obtained from the completely randomized experiment (CRD) met all assumptions of analysis of variance (ANOVA), and were subjected to two-way ANOVA to identify significant difference among treatments. Interaction between fertilizer products and days were worked out for assessing the treatment effect on P release. Duncan's Multiple Range Test (DMRT) test was used for multiple comparisons among the treatments at P =0.05 using R software.

RESULTS AND DISCUSSION

Physical and chemical properties of experimental soil

The soil has a pH of 9.6 and belongs to textural class 'Loam' with 46.6, 34.0 and 19.4 sand, silt and clay particles, respectively. The soil was categorized as non-saline as the EC was 0.39 $dSm^{-1.}$ Soil organic carbon (OC), nitrogen (N) and potassium (K)contents were rated as low with the values 0.26%,150 and 97.9 $kgha^{-1}$, respectively. The CEC of the soil was 16.9 $cmol(p^{+})kg^{-1}$. The soil sample was in medium fertility status with respect to available P as the P content was estimated to be 14 kg ha^{-1}. The soil sample was found to be high in sodium and has an exchangeable sodium percentage of 44.1 (ESP). The soil sample was found to be deficient in DTPA extractable micronutrients viz. Fe, Cu, Mn, and Zn and valued 2.7, 0.15, 1.04 and0.43$mgkg^{-1}$, respectively.

Effect of oil coating on release behavior of P from fertilizer products

Temporal release of P from OC-DAPs and DAP are represented in Figure 1. It was observed that the release of P from OC-DAPs and DAP followed an increasing trend from 7 to 60 days (Figure 1 A). However, the release of P was far greater from uncoated DAP than coated OC-DAPs. The Uncoated DAP released almost 60% of the applied P by the end of 60 days (Table 2). Release of P from OC-DAPs ranges from 4-11% through outthe study period and were significantly less from uncoated DAP by a huge margin (Figure 1B) . According to Trivedi *et al.,* 2017, the fixation of P in sodic soil is almost nil; rather sodium present in these high pH soils helps in enhancing the availability of P. Hasana *et al.,* 2022 observed a similar trend in a closed incubation study conducted in sodic soil treated with phospho-gypsum amendments. Among the treatments, lowest P release was observed in OC-DAP_9 (Table 2). Products with increased oil content such as OC-DAP_7, OC-DAP_8 and OC-DAP_9 observed the lowest P release (0.515, 0.511 and 0.493, respectively) than those with lesser quantity of the same as in OC-DAP_1 to OC-DAP_6. This could be mainly due to the restricted nutrient release from OC-DAPs due to the polymeric coating of NPO (Ye *et al.,* 2019).

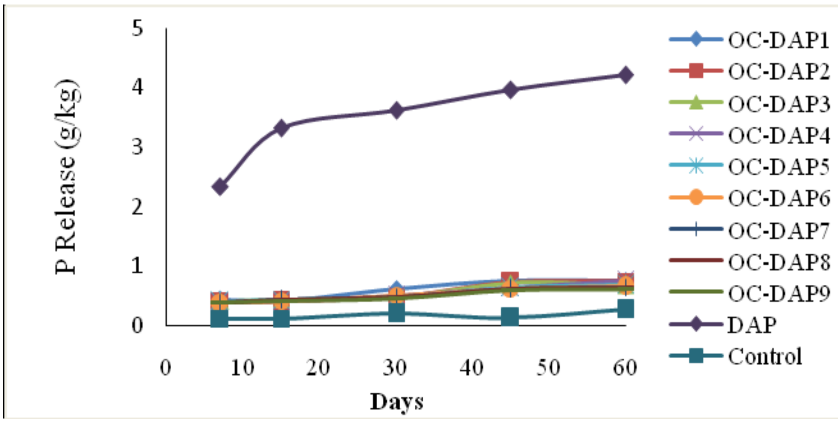

Figure 1 A: Temporal release of P (gkg^{-1}) from fertilizer products

**Treatment details are given in Table 1*

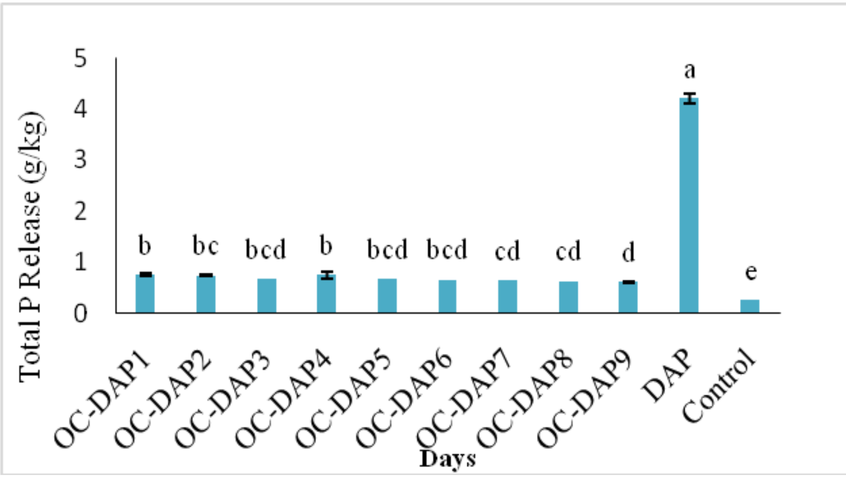

Figure 1 B: Cumulative release of P from fertilizer products in 60 days

**Treatment details are given in Table 1*

Bortoletto-Santos *et al.,* (2016) suggested that coating of urea with castor and soybean oil reduced release of N significantly. Further, Sarkar *et al.,* 2021 has observed that a higher coating percentage of DAP with natural oil resulted in greater reduction of N and P release. Da Cruz *et al.,* 2017 observed that oil-based formulations of coated DAP will lengthen the period of nutrient release and supply nutrients for a longer period of time.

Table 2: Release of P (gkg^{-1}) from synthesized products and DAP insodic soil (Karnal, Haryana)

Days (D)	Sources (S)											Mean
	Oil (mL)+Clay (g)									DAP	Control	
	OC-DAP_1	OC-DAP_2	OC-DAP_3	OC-DAP_4	OC-DAP_5	OC-DAP_6	OC-DAP_7	OC-DAP_8	OC-DAP_9			
7	0.416^{mn}	0.379^{n}	0.416^{mn}	0.388^{mn}	0.408^{mn}	0.394^{mn}	0.393^{mn}	0.387^{mn}	0.378^{n}	2.334^{e}	0.115^{p}	0.547^{E}
15	0.427^{mn}	0.407^{mn}	0.435^{mn}	0.413^{mn}	0.437^{mn}	0.413^{mn}	0.431^{mn}	0.427^{mn}	0.415^{mn}	3.311^{d}	0.119^{p}	0.657^{D}
30	0.622^{ij}	0.488^{lmn}	0.485^{lmn}	0.494^{lmn}	0.491^{lmn}	0.508^{klm}	0.49^{lmn}	0.49^{lmn}	0.457^{mn}	3.611^{c}	0.132^{p}	0.758^{C}
45	0.765^{f}	0.726^{fghi}	0.716^{fghij}	0.631^{hij}	0.639^{ghij}	0.622^{ij}	0.616^{ijk}	0.613^{ijk}	0.597^{jkl}	3.959^{b}	0.2^{op}	0.911^{B}
60	0.764^{f}	0.743^{fgh}	0.676^{fghij}	0.754^{fg}	0.679^{fghij}	0.66^{fghij}	0.644^{ghij}	0.637^{ghij}	0.617^{ijk}	4.207^{a}	0.27^{o}	0.968^{A}
Mean	0.599^{B}	0.549^{C}	0.545^{C}	0.536^{CD}	0.531^{CD}	0.519^{CD}	0.515^{CD}	0.511^{CD}	0.493^{D}	3.484^{A}	0.167^{E}	
LSD (P=0.05)	D= 0.030					S= 0.044						
	S×D= 0.099											

**Values followed by different superscript letters in a column and mean values followed by different capital letters are significantly different (P=.05) *Treatment details are given in Table 1*

Effect of clay coating on release behavior of P from fertilizer products

It was also observed that P release decreased with increased clay content irrespective of the quantity of oil added. In the case of OC-DAP_1 to OC-DAP_3 which has 5 mL oil in all the three combinations but varying clay content, a declining trend in P release is observed with increasing clay content (0.599, 0.549 and 0.545 g kg^{-1}, respectively) and a similar trend was observed in other OC-DAPs too where 7.5 and 10mL oil were used (Table 3). Neto *et al.,* 2023 quoted that a CRF formulated using granulated urea, carnauba wax and Na-bentonite observed lower cumulative release of nitrogen than standard fertilizers. He claimed that bentonite clay is a promising material for formulation of urea based controlled-release fertilizers along with carnauba wax. The consistent and controlled release of P from OC-DAPs make these potential products to be used as slow/controlled-release fertilizers as they have greater longevity for release than commercial DAP, will supply nutrients for longer period, thereby increase nutrient use efficiency (NUE). The sustained supply of P from OC-DAPs ensure that the fertilizer applied meets the requirements of plants in a consistent and effective manner without wastage of resources (Trenkel *et al.,* 2021).In conclusion, this research contributes to the development of innovative, sustainable, cost-effective P fertilizers for increasing crop yields. The OC-DAPs are having high slow-release property as compared to the uncoated DAP. The simple execution of the procedure followed to prepare these novel fertilizers and the cost-effective materials used would help in curtailing the cost involved. Furthermore, the fact that they are made of non-toxic and biodegradable materials contribute to their long-term viability and potential for use in agriculture. Controlled and sustained release of P from CRFs like OC-DAP could help in reducing the recommended dose of P to crops and there by helps in conserving resources. Hence, inclusion of these products in P management protocol of cultivated crops need further evaluation involving various crops and soils.

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