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Phosphorus Release from Rock Phosphate as Influenced by Organic Acid Loaded Nanoclay Polymer Composites in an Alfisol

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Abstract The aim of the present study was to develop a strategy to solubilize low-grade rock phosphate (RP) from Purulia and Udaipur through organic acids loaded nanoclay polymer composites (NCPC) and see their effectiveness as source of P. An incubation experiment was conducted under laboratory condition to study the release pattern of P in an Alfisol from Jharkhand amended with various RPs treated with organic acid loaded NCPC for 90 days. The RPs were applied at a dose of 0, 50 and 100 mg P kg^{-1} soil, along with the organic acid loaded NCPC having 10 % clay which was applied at a dose of 0, 20 and 40 mg organic acid kg^{-1} soil. The incubation experiment showed a positive impact of the organic acids in their ability to release P from all the RP sources, and oxalic acid performed better over citric acid in solubilizing P from RPs. The two indigenous RPs maintained almost comparable available P in soil throughout the period of incubation. With increase in levels of P application, there was an increase in the amount of release of P from both the RPs. Similarly, with the increase in levels of organic acid both Udaipur and Purulia RPs showed increase in the available P in soil. This study demonstrated that availability of P from low-grade indigenous RP could be improved with the interventions of organic acid loaded NCPC which could be used as P-fertilizer and reduce the dependence on commercial fertilizers like DAP.

Keywords Rock phosphate · Organic acid · Release of P · Bray's-P · Nanoclay polymer composites

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Introduction

Phosphorus (P) is one of the major essential nutrient elements to sustain all forms of life and indispensable for the functioning of virtually every living cell. Despite it being the 11th most abundant element in the earth's crust, its complex chemistry in soil makes it highly deficient nutrient element in most of the arable soils across the globe. Only 0.1 % of the total P in the soil is available for uptake by plants [1] because of its fixation as various insoluble compounds depending upon the soil pH. In the Indian context, about 49.3 % districts are reported to have low available P content based on 9.6 million soil test values [2]. In another study it is reported that 42 % of the total districts in India are low in available P status [3]. Thus, application of P-fertilizers to maintain the soil fertility and sustain crop productivity becomes imperative in today's input intensive agriculture.

Rock phosphate (RP), the backbone of the P-fertilizer industry, is a highly priced commodity in the world market due to concentrated distribution of the reserves across the globe. India, the largest importer of high-grade RP has been recently facing the burning impact of increased prices of RP as well as diammonium phospate (DAP) as evident from the recent statistics of FAI, which indicates a 15 % decline in DAP consumption in the year 2013–2014. Therefore, research priorities are being directed towards finding alternative sources of P-fertilizers like indigenous RP. In this regard India is fortunate to have about 260 million tonnes (Mt) reserves of RP [4], while according to another estimate, about 296.3 Mt of total resource of RP is available in India [5], out of which only 34.8 Mt accounts for the reserve portion and 261.5 Mt remaining resources. Of the total resources 36 % is concentrated in Jharkhand and West Bengal (mainly from Purulia) and 30 % in

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Udaipur (Rajasthan). However, most of the RP of Indian origin is of poor quality (low-grade) and are not suitable as raw materials for conventional P-fertilizer production [6]. Also, the solubilization of RP requires proton (H^+) which can be obtained through chemical or microbial intervention. Organic acids generally responsible for P solubilization in the rhizosphere could be used as a P solubilizer without having any harm on the environment. Further, effectiveness of nanoclay polymer composites (NCPC) in agriculture to improve soil moisture retention capacity and improving plant growth has been assessed in several investigations [7]. The increasing use of engineered nanoparticles in consumer and industrial products has also aroused global concern regarding their fate in biological systems [8]. Thus, the present investigation was oriented to utilize organic acids viz. oxalic and citric acid loaded in nanoclay polymer composites (OA-NCPC and CA-NCPC) as a solubilizer of indigenous RPs from Udaipur and Purulia along with an exogenous RP from Gafsa in an Alfisol, and to study the P release in soil over a period of 90 days.

Material and Methods

Rock Phosphate and Their Characterization

Three RPs namely, Udaipur RP (URP) from Rajasthan State Mines and Minerals Ltd. Udaipur, Rajasthan, India and Purulia RP (PRP) from West Bengal Mineral Development and Trading Corporation Ltd., Purulia, West Bengal, India and Gafsa RP (GRP) from Tunisia were used for the present study. The URP and PRP are indigenous RP sources belonging to low-grade category, while GRP is a high-grade one.

Samples of RPs were analyzed for total P, water soluble P, citrate soluble P and citrate insoluble P as per the procedure outlined by Fertiliser (Control) Order [9]. The initial characterization showed that GRP had very high content of total P (12.0 %) as compared to 9.87 and 8.81 % in case of PRP and URP, respectively. Similarly, water soluble and citrate soluble P contents in GRP are higher than PRP and URP.

Preparation and Characterization of Nanoclay Polymer Composite

The nanoclay polymer composite (NCPC) was prepared using commercially available bentonite clay (10 % clay) along with acrylic acid and acrylamide [10]. Laboratory grade acrylic acid, acrylamide, ammonia and water were reacted in a four necked flask in a nitrogen atmosphere to obtain 60 % neutralization. Commercial bentonite clay was

added @10 % on w/w basis. The final product obtained was dried at 100 °C and ground to pass through 50–60 mesh sieve. The NCPC was characterized for the presence of various functional groups by Fourier transformation infrared spectroscopy (FTIR), for its surface morphology by using scanning electron microscopy (SEM) and electron diffraction X-ray (EDX) was done to see the elemental composition of the NCPC. Following this laboratory grade oxalic and citric acid (ammonium oxalate and ammonium citrate) was loaded in the NCPC @ 2 % w/w basis to obtain OA-NCPC and CA-NCPC.

Experimental Soil and Analyses

Bulk surface (0–15 cm) soil was collected from the experimental farm of Zonal Research Station, Darisai, Jharkhand. The soil was selected taking into account its variable amounts of different pools of P, particularly low in available P (P-deficient). Air dried, processed soil samples passed through 2 mm sieve was used for the experiment.

Initial soil samples were analyzed for physicochemical properties. Mechanical composition was determined by hydrometer method [11]. The pH was determined in 1:2 (soil:water) suspension. The electrical conductivity (EC) was determined in the supernatant liquid of the same extracts. Organic carbon content in soil was determined by wet oxidation method of Walkley and Black [12]. The cation exchange capacity (CEC) was determined by ammonium acetate method as described by Jackson [13]. For mineral N (NH_4^+-N + NO_3^--N), moist soil sample was extracted with 2 M KCl solution [14]. The available P in soil was extracted using the Bray and Kurtz No. 1 extractant (0.03 N NH_4F and 0.025 N HCl) for the acid soil [15]. The P content in the extracts was determined using the ascorbic acid blue colour method [16]. Available K was determined by extracting the soil sample with 1 N ammonium acetate and K content in the extracts was measured by a flame photometer. The initial experimental soil was sandy clay loam in texture with sand, silt and clay 67.4, 9.5 and 23.1 %, respectively. The soil had pH 5.14; EC 0.34 dS m^{-1}; CEC 7.6 cmol (p$^+$) kg^{-1}; organic carbon 2.51 g kg^{-1}; mineral N (NH_4^+-N + NO_3^--N) 12.8 mg kg^{-1}; available P 13.5 mg kg^{-1} and available K 60.7 mg K kg^{-1} soil.

Incubation Experiment

Soil samples (100 g each) were weighed into capped plastic bottles. The three RPs were applied @ 0, 50 and 100 mg P kg^{-1} soil, along with the organic acid loaded NCPC at 0, 20 and 40 mg organic acid kg^{-1} soil and mixed thoroughly. Distilled water was added to maintain the soil moisture at 50 % of the field capacity. An absolute control

receiving no external sources of fertilizer, and a standard check as DAP @ 50 mg P kg^{-1} soil was used to compare the P release from the newly manufactured products. All the samples were maintained in an incubator at a temperature of 30 ± 1 °C. Soil samples were drawn at 7, 14, 30, 45, 60 and 90 days after incubation (DAI) and measured for available P with Bray and Kurtz No. 1 solution [15]. The P content in the extract was determined by ascorbic acid blue color method [16].

Statistical Analyses

Statistical analyses of data generated from incubation experiments were carried out using standard analysis of variance [17]. The least significance difference (LSD) between the treatment means was calculated at $P \leq 0.05$.

Results and Discussion

Characterization of NCPC

The functional group characterization of NCPC samples was done using the FTIR spectroscopy. The spectrum (Fig. 1) showed peaks at 3436, 2957, 2926, 1735, 1655, 1165, 1034 and 573 cm^{-1}. Some low intensity sharp peaks were also observed around 1450 and 2346 cm^{-1}. The peak at 3436 cm^{-1} indicated the stretching vibrations of the hydroxyl (OH) group while the peaks between 1655 and 1735 cm^{-1} indicates the stretching vibrations due to the (carbonyl) C=O group present in acrylic acid, as the NCPC is a copolymer of

the acrylic acid and acrylamide. The 1450 cm^{-1} peak is due to the vibrations of NH$_2$ group in the polyacrylamide. The smaller peaks obtained at 1165 and 1034 cm^{-1} are indicative of the CN stretch vibrations, while the peaks around 2957–2855 cm^{-1} are due to CH stretching vibrations.

The NCPC had an irregular and rough surface morphology as evident from the SEM images shown in Fig. 2. At higher magnification level the pore spaces are also visible in the NCPC structure. The EDX spectrum (Fig. 3) of the NCPC indicated the presence of carbon, oxygen, aluminium and silicon, indicating the presence of bentonite clay along with the acrylic acid and acrylamide polymer.

Incubation Study

The incubation study was carried out over a period of 90 days with the presumed hypothesis that during this period most of the P present in the RP material would be solubilized by the action of organic acids released from the NCPC which in turn, could be utilized by most of the annual crops. The data emanated from the incubation study as evident from the release of P from RP treated with organic acid loaded NCPC during different period of incubation are present in Tables 1 to 6.

Effect of Organic Acid Loaded NCPC on P Release from RP at 7 DAI

The P release pattern from various RPs after 7 days of incubation (Table 1) revealed that the organic acid loaded NCPC showed a distinct trend where oxalic acid loaded
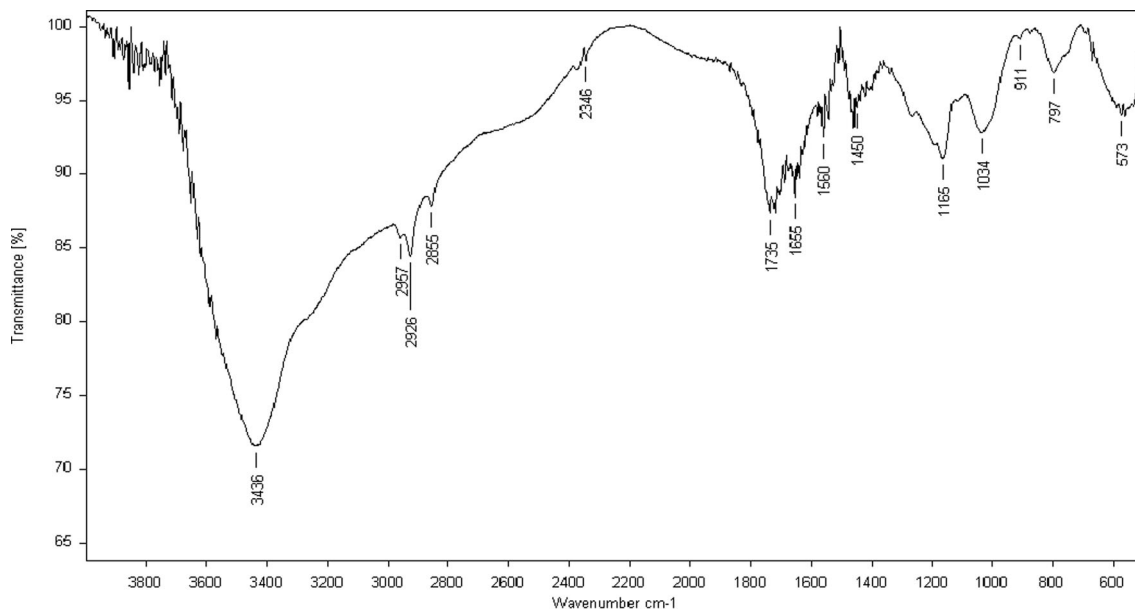

Fig. 1 Fourier transformation infrared spectroscopy (FTIR) spectrum of nanoclay polymer composite
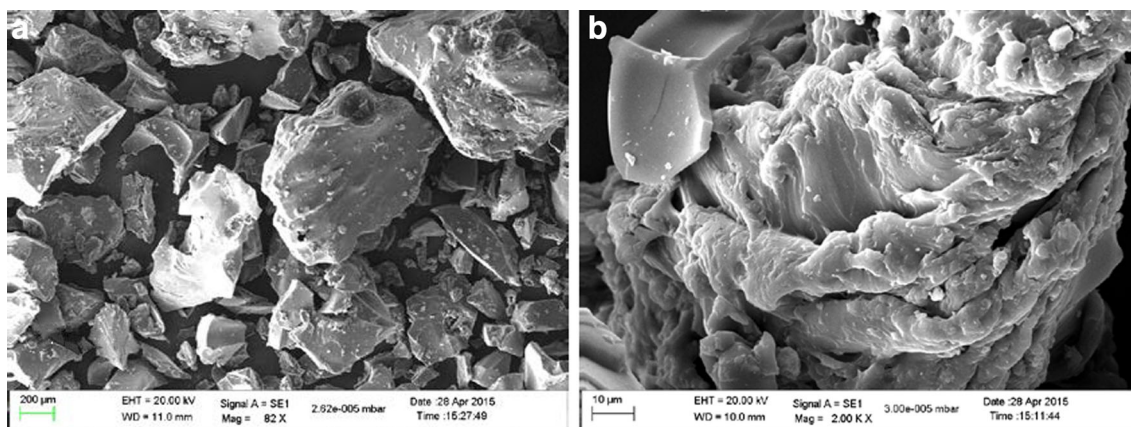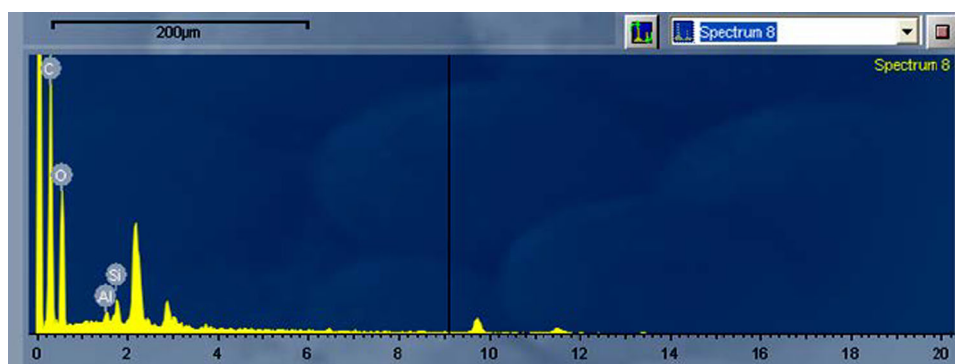
Fig. 2 Scanning electron microscopy (SEM) images of the nanoclay polymer composite at 100 μm scale (**a**) and 10 μm scale (**b**)

Fig. 3 Electron diffraction X-ray (EDX) spectrum of nanoclay polymer composite

NCPC (OA-NCPC) performed better over citric acid loaded NCPC (CA-NCPC). However, the difference was significant only in case of URP while for PRP and GRP they were at par. For both OA-NCPC and CA-NCPC, the increment in the acid doses from LA_0 to LA_{40} led to significant increment in the available P status in soil, but only at LA_{20} level the OA-NCPC showed prominently better P solubilization capacity as compared to CA-NCPC. There was no significant impact of increment in acid dose on P release from GRP, but for URP and PRP it did have significant effect. The absolute control with no externally added P source showed the lowest available P in soil, which was significantly lower than the treatments where no external P source had been added but was supplied with organic acid loaded NCPC. Among the RPs, GRP was superior over DAP, but PRP and URP were statistically inferior in terms of available P content in the soil.

Effect of Organic Acid Loaded NCPC on P Release from RP at 14 DAI

The P release at 14 DAI (Table 2) showed that for all the three RP sources, the OA-NCPC was superior in its capability to release P from them as compared to CA-NCPC.

With the increase in levels of organic acid applied through NCPC, the available P content in the soil showed a significant increment for both the organic acids. When GRP was used as a P source the P released declined sharply with the increase in acid dose from 0 to 40 mg kg^{-1} but not so for either PRP or URP. Even when there was no addition of any P sources, the organic acid loaded NCPC were capable of maintaining a higher P content in soil as compared to control. It was observed that, in general, at 14 DAI the P content in the soil was higher as compared to the values obtained at 7 DAI, irrespective of sources of P, levels of P and levels of acid used.

Effect of Organic Acid Loaded NCPC on P Release from RP at 30 DAI

At 30 days of incubation (Table 3) the P content in soil declined sharply as compared to the level maintained during 14 DAI which might be due fixation of the released P in soil. For PRP, the effect of OA-NCPC proved to be significantly better over CA-NCPC in terms of maintaining a higher P level in the soil, while for URP, the reverse trend was observed. For GRP, both the acid proved to be equally effective in maintaining the available P status in soil. The

Table 1 Release of P from RPs (mg P kg^{-1}) at 7 days after incubation as affected by organic acid loaded NCPC

Treatment	Organic acid loaded NCPC (NCPC-product)		Levels of P (LP) (mg P kg^{-1})			Levels of organic acid (LA) (mg kg^{-1})			Mean
	OA-NCPC	CA-NCPC	LP$_0$	LP$_{50}$	LP$_{100}$	LA$_0$	LA$_{20}$	LA$_{40}$	
Sources of P									
PRP	19.7	19.9	17.1	18.6	19.8	15.9	19.1	20.2	18.5
URP	20.1	19.3	17.1	19.5	19.7	15.7	19.0	20.6	18.6
GRP	24.5	24.1	17.1	24.3	29.3	19.8	24.2	24.5	23.2
Levels of organic acid (mg kg^{-1})									
LA$_0$	17.1	17.1	13.1	18.2	20.1				
LA$_{20}$	21.1	20.4	17.2	21.3	23.8				
LA$_{40}$	21.9	21.6	19.7	22.1	23.5				
Levels of P (mg kg^{-1})									
LP$_0$	18.3	18.5							
LP$_{50}$	22.1	21.3							
LP$_{100}$	24.1	23.2							
Mean	21.5	21.0	16.7	20.5	22.5	17.1	20.8	21.8	20.1
DAP	19.3								
Control	13.1								
CD ($P = 0.05$)									
RP	0.62				NCPC-product × RP			0.87	
NCPC-product	0.50				RP × LP			1.07	
LP	0.62				RP × LA			1.07	
LA	0.62				NCPC-product × LP			0.87	
Control versus rest	0.35				NCPC-product × LA			0.87	
DAP versus treated	0.35				LA × LP			1.07	

mean values of P solubilized due to the effect of the organic acid loaded NCPC on the RPs indicated that there was no significant difference in their performance on the 30 DAI. It is evident that all the RPs did not show similar response in releasing P due to the increasing level of organic acids as applied through NCPC (Table 3). The dose of 20 mg kg^{-1} irrespective of the acid used was observed to be better as compared to either 0 or 40 mg kg^{-1}.

Effect of Organic Acid Loaded NCPC on P Release from RP at 45 DAI

The release of P after 45 days of incubation (Table 4) also showed similar trend where OA-NCPC helped to maintain a higher value of available P as compared to CA-NCPC. The available P status in soil due to PRP showed a significant difference between the OA-NCPC and CA-NCPC. For URP, the OA-NCPC and CA-NCPC maintained equal content of available P in soil. In case of GRP, the CA-NCPC was found to be better as compared to OA-NCPC. The increment in organic acid level on P release pattern from various RPs showed similar trend as

observed in the previous results. Similarly, enhancement in the values of available P in soil after 45 DAI (Table 4) was recorded after the P levels were increased from 0 to 100 mg kg^{-1}.

Effect of Organic Acid Loaded NCPC on P Release from RP at 60 DAI

The results of P release at 60 DAI (Table 5) showed that for all the three RP sources the OA-NCPC performed significantly better than the CA-NCPC. The mean available P maintained by OA-NCPC was higher (16.1 mg P kg^{-1}) as compared to CA-NCPC (15.5 mg kg^{-1}). The organic acid loaded NCPCs were able to maintain available P status significantly higher than that maintained by the DAP source (10.1 mg P kg^{-1}). Compared to the P present in soil solution at 45 DAI, there was a sharp decline observed at 60 DAI in all the treatments. Both the organic acid loaded NCPC showed an increment in the available P status in soil as there was an increase in the applied P doses from LP$_0$ to LP$_{100}$. When the effect of the levels of organic acid applied through NCPC was considered, a concurrent rise in the available P status was observed with the corresponding rise

Table 2 Release of P from RPs (mg kg^{-1}) at 14 days after incubation as affected by organic acid loaded NCPC

Treatment	Organic acid loaded NCPC (NCPC-product)		Levels of P (LP) (mg P kg^{-1})			Levels of organic acid (LA) (mg kg^{-1})			Mean
	OA-NCPC	CA-NCPC	LP$_0$	LP$_{50}$	LP$_{100}$	LA$_0$	LA$_{20}$	LA$_{40}$	
Sources of P									
PRP	18.7	18.2	16.8	19.6	19.0	16.2	19.0	20.2	18.5
URP	18.8	17.8	16.8	19.2	19.1	15.5	19.8	19.6	18.3
GRP	34.4	33.0	16.8	35.7	48.6	30.2	37.0	33.8	33.7
Levels of organic acid (mg kg^{-1})									
LA$_0$	20.6	20.6	14.2	21.8	26.0				
LA$_{20}$	28.2	26.4	18.2	26.4	26.2				
LA$_{40}$	27.5	24.7	18.0	31.2	29.4				
Levels of P (mg kg^{-1})									
LP$_0$	16.5	17.1							
LP$_{50}$	25.8	23.8							
LP$_{100}$	29.6	28.2							
Mean	24.0	23.0	16.8	26.5	27.2	20.6	25.3	24.5	23.5
DAP	18.3								
Control	14.2								
CD (P = 0.05)									
RP	0.89			NCPC-product × RP			1.26		
NCPC-product	0.73			RP × LP			1.54		
LP	0.89			RP × LA			1.54		
LA	0.89			NCPC-product × LP			1.26		
Control versus rest	0.51			NCPC-product × LA			1.26		
DAP versus treated	0.51			LA × LP			1.54		

in organic acid level in case of the different RP sources (Table 5).

Effect of Organic Acid Loaded NCPC on P Release from RP at 90 DAI

The P release from RPs at 90 DAI (Table 6) showed that for PRP, the OA-NCPC was able to solubilize more P and consequently maintain a higher P status as compared to CA-NCPC. However, in case of URP and GRP, CA-NCPC was observed to be a better performer as a P-solubilizer over OA-NCPC. For URP and PRP the increase in the organic acid level showed a significant leap in the available P status of the soil, but for the high-grade GRP there was always a depression in the available P status as the acid level rose from LA$_{20}$ to LA$_{40}$. The increment in P levels on 90 DAI (Table 6) showed similar trend as observed previously. The LP$_0$ recorded the lowest content of available P in soil while the LP$_{100}$ recorded the maximum available P in soil. Irrespective of the source of P used as RPs, the increment in P level always showed a beneficial effect on the available P status of soil even after 90 DAI.

Phosphorus Release Pattern as Affected by Various Factors During Incubation Period

The P release pattern obtained over the period of 90 days as affected by three RPs as source of P along with DAP and absolute control (Fig. 4a) showed the superior performances of the high-grade GRP throughout the incubation period as compared to the other P sources including DAP. When the two indigenous RPs were compared with DAP, the available P status maintained by them were in close proximity with each other and both URP and PRP maintained similar content of available P. The P release pattern as affected by the organic acid loaded NCPCs and its comparison with the DAP and absolute control (Fig. 4b) revealed that the release of P from the various sources did not show a steady increasing pattern but rather an alternate rise and fall in the available P content in the soil was measured. During 7–45 DAI, the OA-NCPC performed better over CA-NCPC in terms of P solubilization, but on the 60 DAI they had the same mean values of the P released, while at 90 DAI there was a slight increase in the P release due to CA-NCPC as compared to OA-NCPC. The

Table 3 Release of P from RPs (mg kg^{-1}) at 30 days after incubation as affected by organic acid loaded NCPC

Treatment	Organic acid loaded NCPC (NCPC-product)		Levels of P (LP) (mg P kg^{-1})			Levels of organic acid (LA) (mg kg^{-1})			Mean
	OA-NCPC	CA-NCPC	LP$_0$	LP$_{50}$	LP$_{100}$	LA$_0$	LA$_{20}$	LA$_{40}$	
Sources of P									
PRP	12.0	11.2	10.1	11.9	12.8	9.6	12.7	12.5	11.6
URP	11.5	12.0	10.1	11.4	13.8	9.9	12.4	13.0	11.8
GRP	21.4	21.5	10.1	20.7	33.6	17.1	25.2	22.1	21.5
Levels of organic acid (mg kg^{-1})									
LA$_0$	12.2	12.2	8.1	11.7	16.9				
LA$_{20}$	15.9	17.5	11.5	16.2	22.4				
LA$_{40}$	16.8	15.0	10.6	16.2	20.8				
Levels of P (mg kg^{-1})									
LP$_0$	9.4	10.7							
LP$_{50}$	14.9	14.5							
LP$_{100}$	20.7	19.5							
Mean	15.0	14.9	10.1	14.7	20.0	12.2	16.8	15.9	14.9
DAP	14.0								
Control	8.1								
CD (P = 0.05)									
RP		0.41				NCPC-product × RP		0.58	
NCPC-product		0.34				RP × LP		0.71	
LP		0.41				RP × LA		0.71	
LA		0.41				NCPC-product × LP		0.58	
Control versus rest		0.25				NCPC-product × LA		0.58	
DAP versus treated		0.25				LA × LP		0.71	

DAP treatment throughout the incubation period showed a poorer performance than the organic acid loaded NCPC. When the overall impact of the levels of organic acid applied through NCPC was considered (Fig. 4c) results indicated that there was not much difference observed between the LA$_{20}$ and LA$_{40}$. At 7 and 90 DAI, the LA$_{40}$ was better than LA$_{20}$, but for all the other days LA$_{20}$ was better than LA$_{40}$. The LA$_0$ showed the least value of available P content in soil but not lower than the absolute control which showed the poorest performance in terms of P solubilization and maintaining the available P status in soil throughout the incubation period of 90 days. As far as the impact of various P levels on the available P status in soil is concerned (Fig. 4d), it is clearly seen that throughout the incubation period, the LP$_{100}$ showed the peak content of available P as compared to the LP$_{50}$ or LP$_0$. Also, the DAP showed lower values of available P as compared to LP$_{50}$ and LP$_{100}$ but higher than the LP$_0$ or the absolute control. At 30 and 60 DAI, the amounts of P released were the lowest irrespective of the levels of P application.

The P dissolution from RP was measured indirectly as the amount of available P present in the soil solution. The three RPs showed differential capability to be solubilized by the two organic acids loaded NCPC. The nature of RPs used in the study as well as the physicochemical properties of soil have a major influence on the amount of P solubilized from the various RPs [18, 19]. In the present study, the GRP used is an exogenous RP from Tunisia which is a high-grade RP as evident from its total P content (12.0 % P or 27.5 % P$_2$O$_5$), while the PRP and URP are of low-grade quality having only 9.87 % P (or 22.6 % P$_2$O$_5$) and 8.81 % P (or 20.2 % P$_2$O$_5$), respectively. Results in the incubation study revealed that the soil treated with GRP maintained higher concentration of available P throughout the incubation period as compared to both the indigenous RPs, which might be related to its inherent higher P content in the former source. Reports also suggest that the GRP generally falls into the category of sedimentary RPs which generally has higher reactivity than the igneous RP sources [18].

The P dissolution from RPs is also highly dependent on the soil properties, particularly the soil pH and the Ca ion

Table 4 Release of P from RPs (mg kg^{-1}) at 45 days after incubation as affected by organic acid loaded NCPC

Treatment	Organic acid loaded NCPC (NCPC-product)		Levels of P (LP) (mg P kg^{-1})			Levels of organic acid (LA) (mg kg^{-1})			Mean
	OA-NCPC	CA-NCPC	LP$_0$	LP$_{50}$	LP$_{100}$	LA$_0$	LA$_{20}$	LA$_{40}$	
Sources of P									
PRP	22.0	20.3	18.1	22.1	23.2	15.8	23.0	24.6	21.1
URP	21.9	21.5	18.1	22.7	24.4	15.7	23.9	25.6	21.7
GRP	43.1	44.3	18.1	47.9	65.1	37.7	48.9	44.4	43.7
Levels of organic acid (mg kg^{-1})									
LA$_0$	23.0	23.0	10.6	25.2	33.2				
LA$_{20}$	31.2	32.7	21.3	35.1	39.5				
LA$_{40}$	32.7	30.4	22.3	32.5	39.3				
Levels of P (mg kg^{-1})									
LP$_0$	18.4	17.7							
LP$_{50}$	30.9	30.9							
LP$_{100}$	37.7	37.4							
Mean	29.0	28.7	18.1	30.9	37.3	23.1	31.9	31.5	28.9
DAP	22.5								
Control	10.6								
CD ($P = 0.05$)									
RP		1.17				NCPC-product × RP		1.66	
NCPC-product		0.96				RP × LP		2.03	
LP		1.17				RP × LA		2.03	
LA		1.17				NCPC-product × LP		1.66	
Control versus rest		0.68				NCPC-product × LA		1.66	
DAP versus treated		0.68				LA × LP		2.03	

concentration in the soil solution [20]. The general reaction indicating the solubilization of apatite in soil is given by:

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \quad (1)$$

From Eq. 1, it is evident that the protons (H$^+$) play a major role in the dissolution of P from RPs. The experimental soil under study is an Alfisol from Jharkhand with a pH of 5.4 and low available P status of only 13.4 mg kg^{-1} of Bray's P in the soil solution. Thus, addition of RP as a P source resulted in increased concentration of available P in soil solution which was comparable to the amount of P maintained by the conventional DAP fertilizer. But the mean values of available P due to the different RP sources showed that DAP performed significantly better over the indigenous RP sources throughout the incubation period except at 60 DAI where RP was found better than DAP because of more fixation of P from water soluble P sources. However, the GRP performed better as a P source than DAP. Similar trend of DAP was observed when compared with

Jhamarkotra RP over a 100-day incubation period in an alkaline soil by Begum et al. [21].

The impact of the organic acid loaded NCPC in enhancing the P solubilization from RP sources is promising. The OA-NCPC showed a superior performance over CA-NCPC during the initial stages till 45 DAI, after which the CA-NCPC showed better P solubilization capacity. The P dissolution capacity of the low molecular weight organic acids are well documented and almost 10–1000 folds enhancement in the soil solution P concentrations have been reported due to the presence of organic acid anions like citrate, oxalate and malate [22–25]. Similar reports were also presented by Kpomblekou and Tabatabai [26] and they reported oxalic acid to be the most effective in releasing P from the RPs. However, they suggested that the release of P from the low-grade RPs was affected maximum due to organic acids, but in the present study the P release from high-grade GRP was also equally affected by the organic acid loaded NCPC. Taghipour and Jalali [27] reported similar results when they studied the P

Table 5 Release of P from RPs (mg kg^{-1}) at 60 days after incubation as affected by organic acid loaded NCPC

Treatment	Organic acid loaded NCPC (NCPC-product)		Levels of P (LP) (mg P kg^{-1})			Levels of organic acid (LA) (mg kg^{-1})			Mean
	OA-NCPC	CA-NCPC	LP$_0$	LP$_{50}$	LP$_{100}$	LA$_0$	LA$_{20}$	LA$_{40}$	
Sources of P									
PRP	12.4	11.8	9.8	13.7	12.9	11.0	12.3	13.2	12.1
URP	12.4	11.9	9.8	12.3	14.5	10.1	13.3	13.2	12.2
GRP	23.6	22.8	9.8	25.1	34.6	20.9	26.1	22.6	23.2
Levels of organic acid (mg kg^{-1})									
LA$_0$	14.0	14.0	10.0	14.2	17.9				
LA$_{20}$	16.7	17.7	10.2	19.2	22.3				
LA$_{40}$	16.9	15.7	10.4	17.7	21.8				
Levels of P (mg kg^{-1})									
LP$_0$	9.6	10.1							
LP$_{50}$	17.2	16.9							
LP$_{100}$	20.9	20.4							
Mean	16.1	15.5	10.2	17.0	20.7	14.0	17.2	16.3	15.8
DAP	10.1								
Control	10.0								
CD ($P = 0.05$)									
RP		0.57				NCPC-product × RP	0.80		
NCPC-product		0.46				RP × LP	0.98		
LP		0.57				RP × LA	0.98		
LA		0.57				NCPC-product × LP	0.80		
Control versus rest		0.32				NCPC-product × LA	0.80		
DAP versus treated		0.32				LA × LP	0.98		

release from a calcareous soil in western Iran and oxalic acid was observed to produce the maximum P dissolution, followed by citric acid and finally malic acid.

As already mentioned in Eq. 1, the P release from the RP sources are proton mediated. But when the organic acids come into play it is not only the proton released by organic acids which enhances the P solubilization from RP, but also direct ligand exchange reactions whereby citrate or oxalate replaces the P on the ligand exchange surface or forming complexes with metal ions responsible for binding the P [28]. Since in the present experiment the soils were amended with RPs which is generally Ca-apatite, the performance of OA-NCPC was better over CA-NCPC, because the oxalate is capable of forming very stable insoluble complexes with Ca forming Ca-oxalate, and removes the Ca from soil solution thereby enhancing its P release capacity from RP. Similar observations have also been reported by several workers [29] who found oxalate to be more effective than citrate in releasing P from Ca-phosphates in calcareous soils.

When organic acid dose was increased from 0 to 40 mg kg^{-1}, there was an increase in the concentration of available P status in the soil. Also, for OA-NCPC the enhancement in acid doses showed an increase in the P solubilization, while for CA-NCPC the increase in P solubilization was significant from LA$_0$ to LA$_{20}$, but from LA$_{20}$ to LA$_{40}$ there was generally a negative impact on the P solubilization. This might be due to the fact that the soil is acidic in reaction and has the presence of more Fe^{3+} and Al^{3+} in the soil solution. With the increasing citric acid levels, it may have formed stable complexes with the Fe and Al present in the soil instead of solubilizing P from RP, leading to lower quantity of available P.

The higher P doses led to steady increase in the amount of P solubilized from the RP, and the effect of dose of P was uniform irrespective of the RP used or the organic acid or level of organic acid used in the treatments. The soil was highly P deficient with only 13.4 mg P kg^{-1}, and thus with the increment in the RP doses the concentration of P in soil solution also increased. Kaloi et al. [30] reported similar

Table 6 Release of P from RPs (mg kg^{-1}) at 90 days after incubation as affected by organic acid loaded NCPC

Treatment	Organic acid loaded NCPC (NCPC-product)		Levels of P (LP) (mg P kg^{-1})			Levels of organic acid (LA) (mg kg^{-1})			Mean
	OA-NCPC	CA-NCPC	LP$_0$	LP$_{50}$	LP$_{100}$	LA$_0$	LA$_{20}$	LA$_{40}$	
Sources of P									
PRP	23.2	23.0	19.8	25.2	25.8	15.4	26.4	27.6	23.3
URP	22.6	23.1	19.8	24.4	24.3	14.9	26.3	27.3	22.8
GRP	41.7	42.2	19.8	49.5	56.6	35.6	45.3	44.9	42.0
Levels of organic acid (mg kg^{-1})									
LA$_0$	22.0	22.0	9.0	27.8	29.1				
LA$_{20}$	32.0	33.3	24.6	34.6	38.8				
LA$_{40}$	33.5	33.0	24.4	36.6	38.8				
Levels of P (mg kg^{-1})									
LP$_0$	19.7	18.9							
LP$_{50}$	32.0	34.0							
LP$_{100}$	35.8	35.4							
Mean	29.2	29.4	19.3	33.0	35.6	22.0	32.7	33.3	29.4
DAP	26.1								
Control	9.0								
CD ($P = 0.05$)									
RP		0.99				NCPC-product × RP		1.39	
NCPC-product		0.81				RP × LP		1.71	
LP		0.99				RP × LA		1.71	
LA		0.99				NCPC-product × LP		1.39	
Control versus rest		0.58				NCPC-product × LA		1.39	
DAP versus treated		0.58				LA × LP		1.71	

observations when an incubation study was carried out to see the impact of P doses on the P release in soil.

Results of the present experiment suggests that the P release pattern from all the P sources i.e. DAP as well as the RPs, both indigenous and the exogenous showed alternate increment and decline in the available P status in soil. The maximum concentration of P in the soil solution was recorded during the 45th and 90th day while the 60th day showed the least concentration of the solution P. The results are in contrast to the findings reported by He et al. [31] who observed a steady increase in the amount of P released from 0 to 80 days after incubation from two types of Central Florida RP in an acid sandy soil. Begum et al. [21] also showed that the Olsen P in soil incubated with RPs had a peak value during 14th day after incubation and followed a sharp decline thereafter during the later stages of incubation. The difference in observation in the present study might be due to the impact of the NCPC which are highly porous materials having high water holding capacity. The NCPC along with the loaded acids may have led to the absorption of released P by them during the maximum P release phase as reported in the other studies, followed by the subsequent release during the later period resulting in a peak during the 90th day when generally the P release was observed to be decreased by other workers.

Future Perspective

This study depicting the possibility of solubilization of low-grade RP which is otherwise not used for commercial production of DAP because of their low P content and unsuitable for direct use as P fertilizer in neutral to alkaline soils. However, the present findings needs further study by comparing its efficacy, thereby its monetary benefits, with standard DAP fertilizers using different crops and cropping sequence under field conditions.
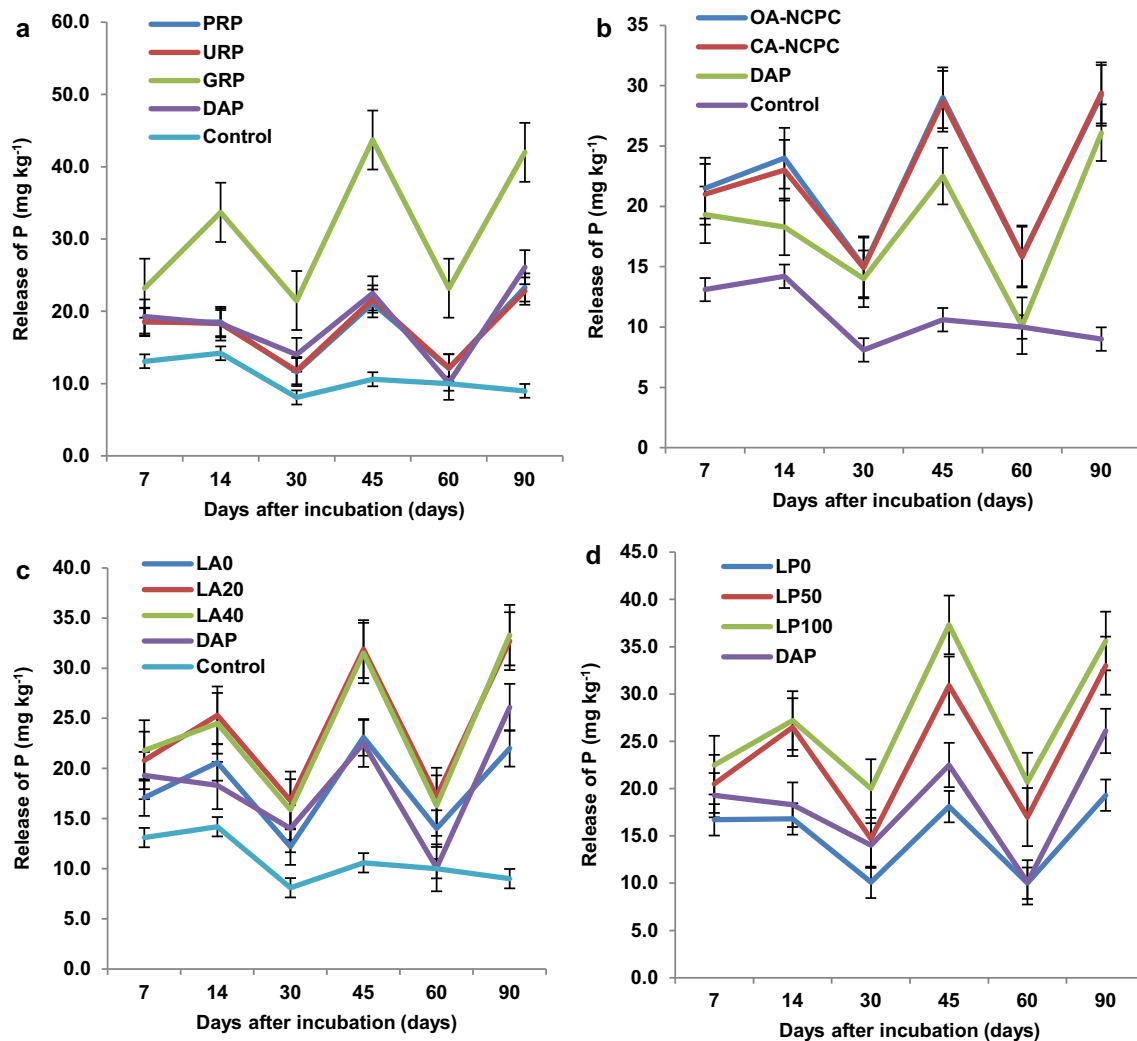
Fig. 4 Release of phosphorus (mg kg^{-1}) from various sources of rock phosphates (**a**) as influenced by organic acid loaded nanoclay polymer composite (**b**) applied at different levels of acid (**c**) and levels of P (**d**) in an Alfisol

Conclusions

This study unfolds an attempt to see the potential of the indigenous RPs as a P source keeping in view the looming perspective of major P scarcity at a global scale. Both the low grade RPs from Purulia and Udaipur were successful in maintaining the available P status in soil over the 90 days incubation period in comparison to the conventional DAP source. Also, the nanoclay polymer composites loaded with oxalic and citric acid showed significant improvement in the soil available P status over the control, particularly at the later stages of incubation which indicates the capacity of the acids to sustain the P release over a longer period, hence synchronizing with the crop growth. When the cumulative impact of organic acid loaded NCPC was compared with DAP, OA-NCPC was able to maintain 22 % more available P and CA-NCPC 20 % more available P over the entire period. The porous nature of nanoclay polymer composites helped to absorb the released P from RP and prevented its immediate fixation thereby causing an alternate crest and trough in the P release pattern during incubation. Overall a new technique of utilizing the indigenous RP sources along with organic acids loaded NCPC was developed which could reduce the dependency of the farmers on costly phosphatic fertilizers like DAP and help in the better utilization of the indigenous RP resources.

Compliance with ethical standards

Conflict of interest The authors have no conflict of interest.

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