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Effect of Organic Acids Loaded Nano Clay Polymer Composites of Rock Phosphate on Growth and Yield of Maize - Cowpea Cropping System

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ABSTRACT

A field experiment was conducted during *Kharif* 2022 in farmer's field at Machanahalli village, Bagepalli taluk, Chikkaballapura district, Karnataka, using RCBD with twelve treatments and three replications to evaluate the effectiveness of organic acids loaded NCPC of RP as a phosphorus source for enhancing the growth and yield attributes in a maize-cowpea cropping sequence. Results revealed that application of phosphorus through organic acids loaded NCPC of nano RP performed significantly better than other treatments in terms of growth and yield of maize and cowpea. Treatment with 100% P through OA-NCPC- nano RP and 100% P through CA-NCPC- nano RP recorded stover yield (82.38 and 82.01 q ha^{-1}), kernel yield (79.08 and 79.01 q ha^{-1}) of maize similar to that of SSP application. Same treatments showed significantly higher grain yield (1581.68 and 1563.90 kg ha^{-1}) and haulm yield (1963.72 and 1934.88 kg ha^{-1}) of residual crop cowpea. The oxalic acid loaded NCPC performed better in most of the cases compared to citric acid loaded NCPC and proved to be a more efficient solubilizer of P from low grade RP. This study could help to utilize low grade RP as a P source for maize-cowpea cropping system, with the interventions of organic acids and reduce the dependence on commercial fertilizers like SSP.

Keywords : Oxalic acid, Citric acid, Low grade nano rock phosphate, Productivity of maize, Growth and yield of cowpea

PHOSPHORUS (P) is the eleventh most abundant element in the Earth's crust and one of the major essential nutrients for crop production. P plays a key role in almost all biochemical processes occurring in the living system and is a constituent of the adenosine tri-phosphate (ATP) which is often referred to as the 'Energy currency of the cell'. But despite its abundance about 43 per cent of the world's arable soil is P deficient which limits crop growth and production (Liu *et al*., 2012). The limitation of P in crop production is attributed to its fixation by iron (Fe) and aluminium (Al) in acidic soils and calcium (Ca) in neutral to alkaline soils (Motsara, 2002). Application of various soluble sources of P-fertilizers such as single superphosphate (SSP), Di ammonium phosphate (DAP) *etc.,* becomes imperative to maintain available P in soil, however higher prices of DAP is a major constraint faced by farmers. A less expensive phosphorus source is rock phosphate - chemically a calcium apatite, generally fluorapatite [$Ca_{10}(PO_4)_6F_2$]. However, this low-grade RP has low water soluble P content and is not suitable for direct application in most of the soils, particularly in neutral to alkaline soil, for annual crops (Roy *et al*., 2015). Therefore, in order to use rock phosphate in all types of soils it needs to blended or treated with specific material which can modify its characteristics.

Solubility of rock phosphate is mainly due to action of acids, either mineral or organic such as oxalic, citric, malic, tartaric, formic *etc*., in soil which is mainly released from root exudates, decomposition of organic matter and microbial decomposition products (Jones, 1998). However, the concentration of these low molecular weight organic acids (LMWOA) in the soil is very low, to the tune of 10^{-3} to 10^{-5} M in soil solution (Kpomblekou and Tabatabai, 2003). Also, their persistence in soil is very less, which is mainly governed by the activity of the microbes, particularly heterotrophs, which utilizes these acids as their substrate for energy source. This lowers the effective concentration of the organic acids in the soil solution and their half-life generally varies from 0.5 to 12 h (Van Hees *et al*., 2003). This restricts the direct application of the LMWOAs to soil, which would then be consumed by microbes rather than serving its purpose as a source of H^+ ions or chelation for RP solubilization. In order to modify the characteristics of rock phosphate a novel technique of using nano clay polymer composite (NCPC) can be adopted to enhance the performance of rock phosphate in all type of soils. The introduction of clay in the hydrogel matrix increases the physical strength of the rock phosphate as well as acts as a barrier towards the release of phosphorus, thereby acting as a controlled release material (Sarkar *et al*., 2013).

Considering all the above points in view, the present investigation was undertaken to utilize two LMWOA *viz*., oxalic acid (OA) and citric acid (CA) loaded in nano clay polymer composite (NCPC), it would protect the acids from microbial decomposition and also increase their persistence time in soil thereby, enhancing the P solubilizing ability of low-grade indigenous rock phosphate. Organic acid loaded NCPCs was used to evaluate their effectiveness as source of P on growth and yield parameters of maize and cowpea grown sequentially.

Material and Methods

A field experiment was conducted during *kharif* 2021 in farmer's field at Machanahalli village, Bagepalli Taluk, Chikkaballapura district, Karnataka, which comes under Agro Climatic Zone - 5, Eastern Dry Zone of Karnataka. The experiment consisted of twelve treatment combinations *viz.,* T_1: Absolute control, T_2: 100% P through SSP, T_3: 100% P through RP, T_4: 100% P through nano RP, T_5 to T_6: 100% P through oxalic acid-loaded rock phosphate (OA-RP), citric acid-loaded rock phosphate (CA-RP) respectively, T_7 to T_8: 100% P through oxalic acid-loaded nano rock phosphate (OA-nano RP) and citric acid-loaded nano rock phosphate (CA-nano RP) respectively, T_9 to T_{10}: 100% P through oxalic acid-loaded nano clay polymer composite of rock phosphate (OA-NCPF-RP), citric acid-loaded nano clay polymer composite of rock phosphate (CA-NCPF-RP) respectively, T_{11} to T_{12}: 100% P through oxalic acid-loaded nano clay polymer composite of nano rock phosphate (OA-NCPF-nano RP) and citric acid-loaded nano clay polymer composite of nano rock phosphate (CA-NCPF-nano RP), respectively. The recommended dosages of nitrogen (150 kg ha^{-1}), potassium (37.5 kg ha^{-1}), $ZnSO_4$ (10 kg ha^{-1}) and FYM (7.5 t ha^{-1}) were applied uniformly across all treatments except the absolute control.

The maize hybrid MAH-14-5 was grown as the main crop during the *rabi* season of 2022. Following its harvest, the same field was utilized to cultivate the cowpea variety *Arka Garima* during the subsequent summer season, relying on the residual soil fertility.

Preparation of Organic Acids Loaded Nano Clay Polymer Composites of Rock Phosphate

Synthesis of Nano Rock Phosphate

Nano rock phosphate synthesis was carried out during 2022 in the Department of Soil Science and

Agricultural Chemistry, College of Agriculture GKVK, UAS, Bangalore. Commercial rock phosphate was passed through a 2-mm sieve and grinded to ≤ 74 µm in a high-speed vibrating sample mill at 1500 rpm for 5 min. This process was performed 5 times. The material then ball-milled in a mixer mill at 1500 rpm for 10 min with a 2 minutes pause in the middle (Adhikari *et al.*, 2014). Synthesized nano RP was subjected to analysis for their chemical and morphological characterization using X-ray Powder Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) and Dynamic Light Scattering (DLS) technique The total phosphorus (P) content in RP and nano RP was 9.84 and 13.46%, respectively.

Loading of Organic Acid into NCPC

The commercially available nano clay polymer composite was loaded with two organic acids *viz*., citric and oxalic acids @ 2% (w/w) loading. The oxalic and citric acid were supplied through laboratory grade ammonium oxalate and ammonium citrate, respectively, which were water soluble and absorbed by the NCPCs and 2 per cent solution of each was prepared in distilled water. After the acid loading, the nano clay polymer composite was dried at 80 °C in a hot air oven, till constant temperature is attained (Roy *et al*., 2015). Thus, after drying and further grinding, the product of oxalic acid loaded nano clay polymer composite (OA-NCPC) and citric acid loaded nano clay polymer composite (CA-NCPC) were blended with RP or nano RP @ 40 mg kg^{-1} of soil.

Initial Physico-chemical Properties of the Soil at Experimental Site

The texture of soil was sandy loam with 77.26 per cent sand, 10.43 per cent silt and 12.31 per cent clay. The soil was neutral (pH: 7.18) in reaction, medium in organic carbon content (5.7 g kg^{-1}) and normal with respect to salt content (0.16 dS m^{-1}). The available nitrogen (280.87 kg ha^{-1}), available phosphorus (34.67 kg ha^{-1}) and available potassium (279.22 kg ha^{-1}) was medium and Ex. Ca 4.81 (Cmol (p+) kg^{-1}), Ex. Mg 3.46 (Cmol (p+) kg^{-1}) and DTPA extractable micronutrients like iron 11.83 mg kg^{-1}, copper 0.74 mg kg^{-1}, manganese 7.82 mg kg^{-1} and zinc 0.67 mg kg^{-1}.

Measurement of Growth and Yield Attributes of Maize and Cowpea

Growth and yield parameters of maize and cowpea were recorded by tagging five plants per treatment, and observations were consistently taken from the same plants throughout the study. Growth observations were recorded at 30, 60 and 90 DAS, as well as at harvest for maize and at 30 and 60 DAS and harvest for cowpea. Plant height was measured from the base of the plant to the base of the fully opened uppermost leaf and expressed in centimeters. The number of leaves per plant was determined by counting fully opened leaves, while the relative chlorophyll content of maize leaves was assessed using a SPAD meter. Cob and pod lengths were measured from the base to the tip for all five cobs and pods collected from tagged plants. The number of rows per cob, kernels per row, pods per plant and seeds per pod were manually counted. Test weight was determined by weighing 100 grains or pods per treatment and expressed in grams.

Results and Discussion

Data on growth parameters of maize presented in Fig. 1a, 2a, 3a and Table 1 indicated that organic acids loaded NCPC of RP application recorded significantly higher growth parameters of maize *viz.,* plant height, number of leaves per plant, leaf area, chlorophyll content and dry matter production than absolute control.

At 30 DAS, plant height ranged from 23.57 cm in the absolute control (T_1) to 34.36 cm in T_2 (100% P through SSP). Among RP treatments, T_{11} (100% P through OA-NCPF- nano RP) (33.33 cm) and T_{12} (100% P through CA-NCPF- nano RP) (33.12 cm) recorded the highest heights, outperforming conventional treatments T_3 (100% P through RP) (28.27 cm) and T_4 (100% P through nano RP) (30.35 cm) (Fig. 1a). Similarly, the number of leaves ranged from 5.41 in T_1 to 7.94 in T_2, with T_{11} (7.47)

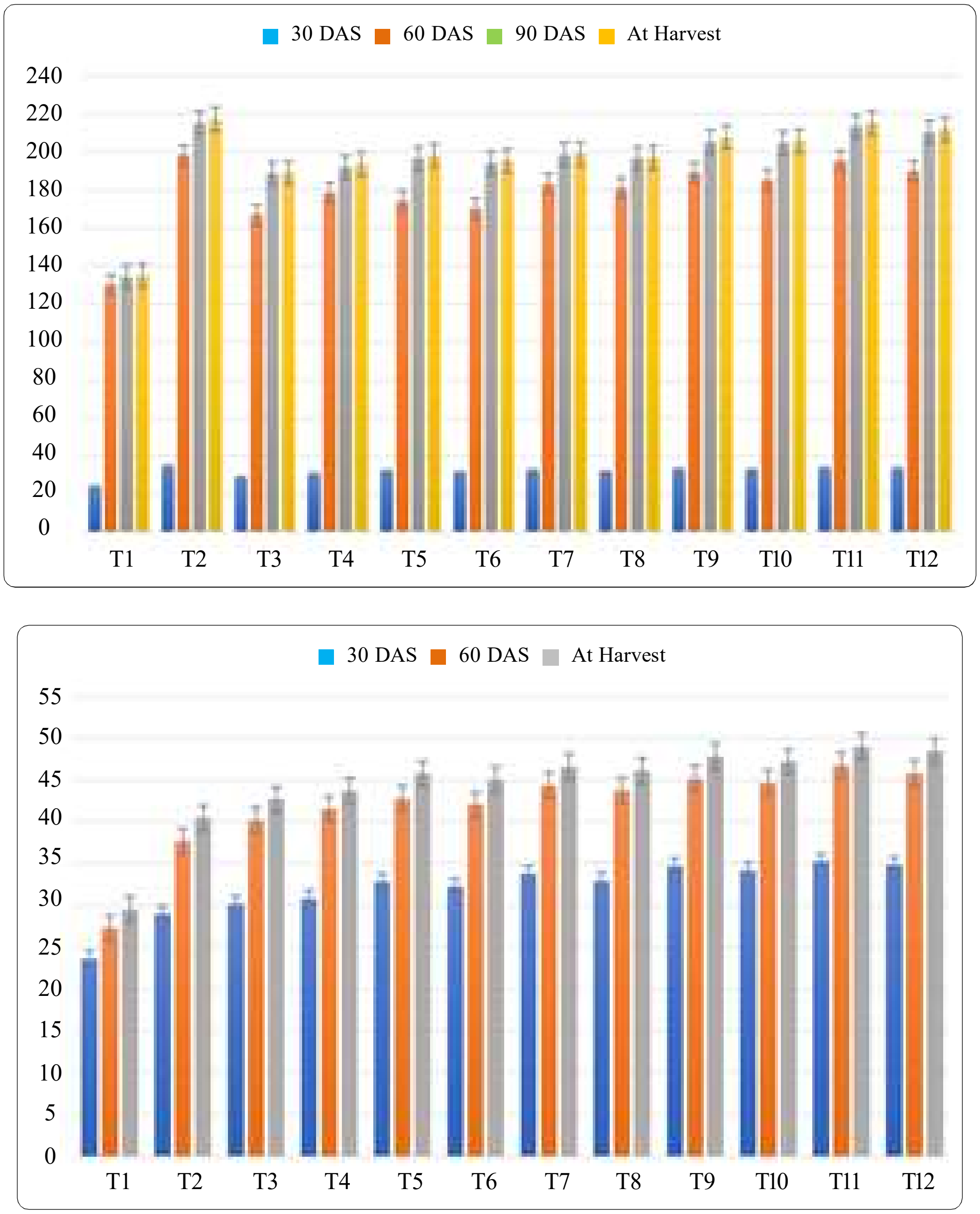
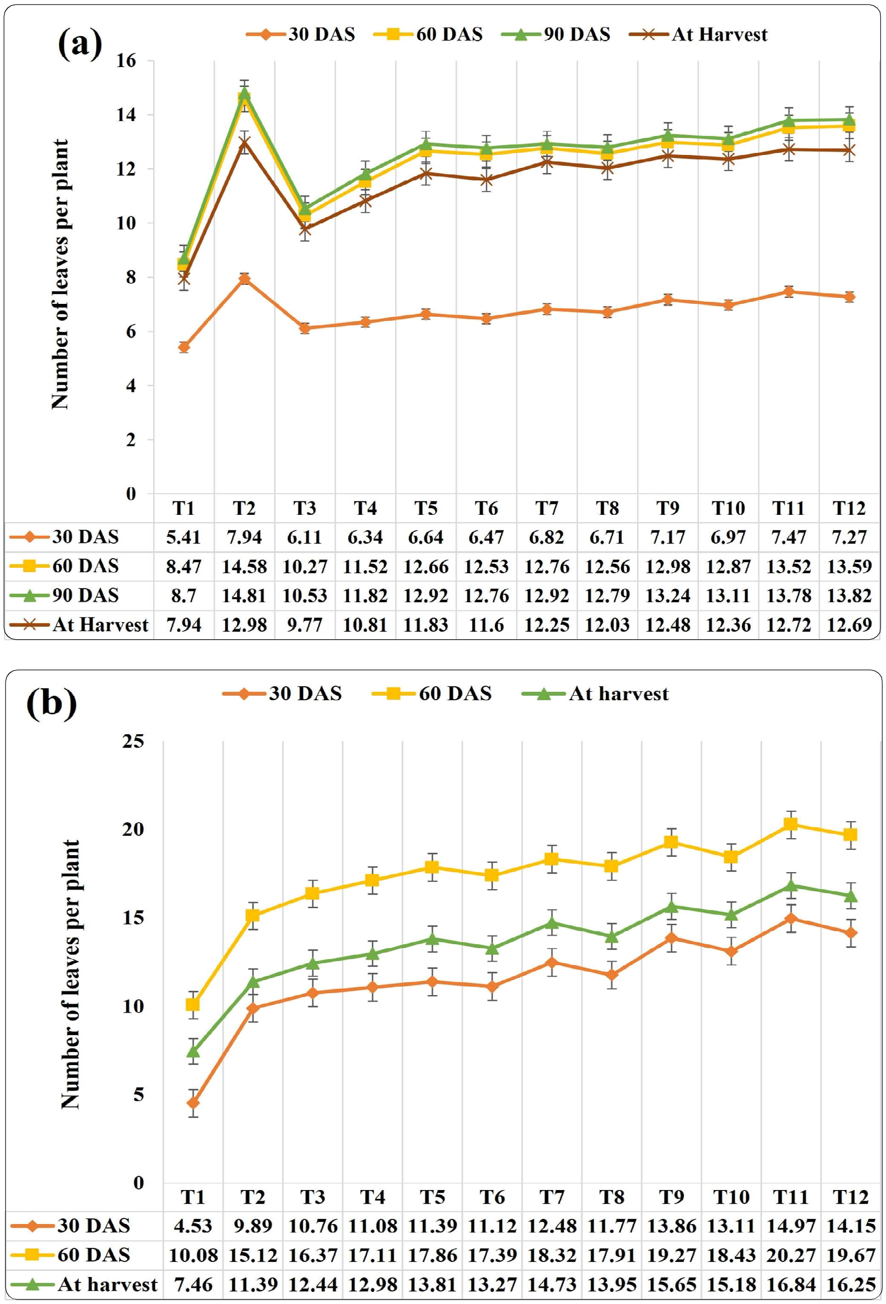


Fig. 1: Effect of organic acids loaded nano clay polymer composites of rock phosphate on plant height (cm) at different growth stages of (a) maize (b) cowpea

and T_{12} (7.27) showing the highest values among RP treatments (Fig. 2a). Leaf area varied from 1738 cm^2 in T_1 to 2502 cm^2 in T_2, with T_{11} (2491 cm^2) and T_{12} (2436 cm^2) outperforming other RP treatments (Fig. 3a). Chlorophyll content followed a similar trend, with T_2 (42.83) and organic acids loaded NCPC of RP treatments like T_{11} (41.35) and T_{12} (41.07) showing the highest values, while T_1 (25.13) recorded the lowest (Fig. 3b). Dry weight ranged from 9.22 g $plant^{-1}$ in T_1 to 11.57 g $plant^{-1}$ in T_2, with T_{11} (11.10 g $plant^{-1}$) and T_{12} (11.01 g $plant^{-1}$) showing higher values among RP treatments, while conventional treatments T_3 (9.65 g $plant^{-1}$) and T_4 (9.72 g $plant^{-1}$) had comparatively lower values (Table 1).

At 60 DAS, T_2 (RDF 100% P through SSP) showed the highest performance across parameters, including plant height (198.55 cm), number of leaves (14.58),



	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12
30 DAS	5.41	7.94	6.11	6.34	6.64	6.47	6.82	6.71	7.17	6.97	7.47	7.27
60 DAS	8.47	14.58	10.27	11.52	12.66	12.53	12.76	12.56	12.98	12.87	13.52	13.59
90 DAS	8.7	14.81	10.53	11.82	12.92	12.76	12.92	12.79	13.24	13.11	13.78	13.82
At Harvest	7.94	12.98	9.77	10.81	11.83	11.6	12.25	12.03	12.48	12.36	12.72	12.69

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12
30 DAS	4.53	9.89	10.76	11.08	11.39	11.12	12.48	11.77	13.86	13.11	14.97	14.15
60 DAS	10.08	15.12	16.37	17.11	17.86	17.39	18.32	17.91	19.27	18.43	20.27	19.67
At harvest	7.46	11.39	12.44	12.98	13.81	13.27	14.73	13.95	15.65	15.18	16.84	16.25

Fig. 2 : Effect of organic acids loaded nano clay polymer composites of rock phosphate on number of leaves per plant at different growth stages of (a) maize (b) cowpea

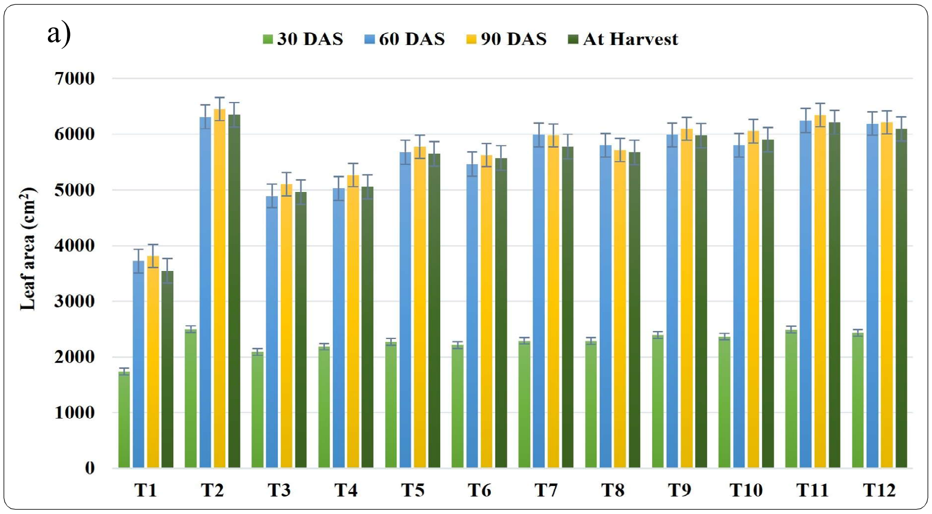
leaf area (6312 cm^2), chlorophyll content (48.60 SPAD) and dry weight (102.85 g plant^{-1}). Among RP treatments, T_{11} and T_{12} demonstrated superior results, with T_{11} recording a plant height of 195.43 cm, leaf area of 6247 cm^2 and dry weight of 102.22 g plant^{-1}, while T_{12} showed comparable values of 190.19 cm, 6191 cm^2 and 101.40 g plant^{-1}, respectively. These treatments also maintained higher SPAD values (47.91 and 47.50) and number of leaves (13.52 and 13.59), while T_1 (absolute control) recorded the lowest values across all parameters.

By 90 DAS, T_2 (RDF 100% P through SSP) exhibited the highest performance across parameters,

TABLE 1

Effect of organic acids loaded nano clay polymer composites of rock phosphate on dry weight (g plant $^{-1}$) of maize and cowpea at different growth stages

Treatment	Maize				Cowpea		
	30 DAS	30 DAS	30 DAS	At Harvest	30 DAS	30 DAS	At Harvest
T_1 : Absolute control	9.22	47.97	67.62	76.92	3.28	5.57	6.47
T_2 : RDF (100% P through SSP)	11.57	102.85	147.50	163.93	4.52	8.39	10.36
T_3 : RDF (100% P through RP)	9.65	89.33	130.72	146.88	4.98	8.94	10.56
T_4 : RDF (100% P through nano RP)	9.72	93.08	134.33	157.35	5.33	9.16	11.06
T_5 : 100% P through OA-RP	9.92	95.46	136.81	159.56	5.97	9.93	11.38
T_6 : 100% P through CA-RP	9.73	94.07	136.00	158.63	5.46	9.52	11.19
T_7 : 100% P through OA- nano RP	10.47	98.28	139.62	159.96	6.42	10.54	11.79
T_8 : 100% P through CA- nano RP	10.43	97.49	139.65	159.22	6.17	10.07	11.42
T_9 : 100% P through OA-NCPF- RP	10.83	99.48	143.54	160.93	7.16	11.26	12.57
T_{10} : 100% P through CA-NCPF- RP	10.67	98.87	142.66	160.87	6.84	10.88	12.26
T_{11} : 100% P through OA-NCPF- nano RP	11.10	102.22	146.55	162.84	7.68	11.75	13.19
T_{12} : 100% P through CA-NCPF- nano RP	11.01	101.40	146.66	161.57	7.25	11.37	12.84
S.Em ±	0.31	3.88	5.64	5.95	0.28	0.45	0.51
CD@5%	0.91	11.38	16.55	17.46	0.82	1.32	1.50



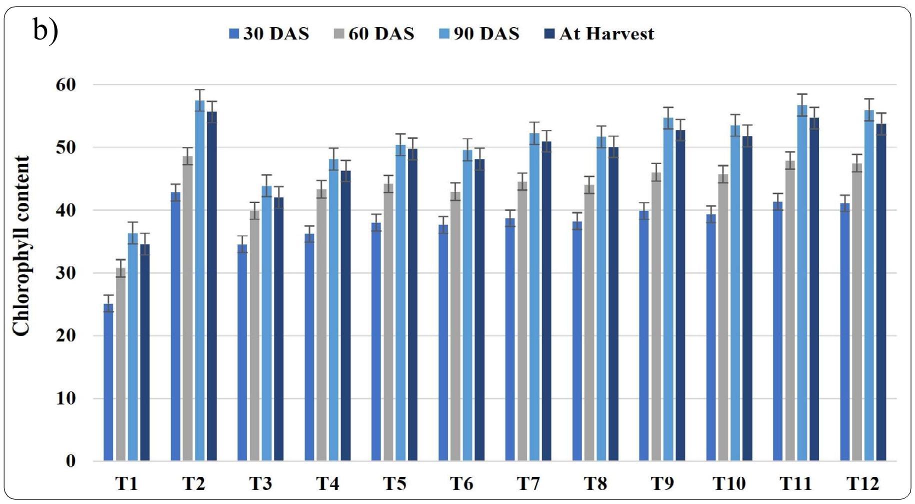


Fig. 3 : Effect of organic acids loaded nano clay polymer composites of rock phosphate on leaf area (cm^2) and chlorophyll content (SPAD meter) of maize at different growth stages

including plant height (215.33 cm), number of leaves (14.81), leaf area (6449 cm^2), chlorophyll content (57.50 SPAD) and dry weight (147.50 g $plant^{-1}$). Among the RP treatments, T_{11} (213.37 cm, 13.78 leaves, 6343 cm^2 leaf area, 56.73 SPAD and 146.55 g $plant^{-1}$ dry weight) and T_{12} (210.61 cm, 13.82 leaves, 6216 cm^2, 55.97 SPAD and 146.66 g $plant^{-1}$) performed exceptionally well. T_9 and T_{10} also recorded significant values, surpassing conventional treatments such as T_3 (130.72 g $plant^{-1}$ dry weight) and T_4 (134.33 g $plant^{-1}$). The absolute control (T_1) consistently recorded the lowest values across all parameters.

At harvest, T_2 (RDF 100% P through SSP) recorded the highest plant height (217.44 cm), followed by T_{11} (215.20 cm) and T_{12} (212.09 cm). NCPC treatments, including T_9 (207.71 cm) and T_{10} (205.95 cm), also outperformed conventional sources like T_3 (189.24 cm) and T_4 (193.72 cm). T_1 (absolute control) had the shortest plants (135.12 cm). Regarding other growth parameters, T_2 also recorded the highest number of leaves (12.98), leaf area (6348 cm^2), SPAD value (55.61) and dry weight (163.93 g $plant^{-1}$). Among NCPC treatments, T_{11} (162.84 g $plant^{-1}$) and T_{12} (161.57 g $plant^{-1}$) showed higher dry weights compared to conventional treatments (T_3: 146.88 g $plant^{-1}$ and T_4: 157.35 g plant^{-1}). T_1 consistently exhibited the lowest values across all parameters.

The residual effect of organic acids loaded nano clay polymer composites of rock phosphate on plant height (Fig. 1b), number of leaves (Fig. 2b) and dry weight (Table 1) of cowpea varied significantly across treatments at different growth stages.

At 30 DAS, the highest values for plant height (35.24 cm), number of leaves (14.97) and dry weight (7.68 g plant^{-1}) were recorded in T_{11} (100% P through OA-NCPF-nano RP), followed by T_{12} (34.83 cm, 14.15 and 7.25 g plant^{-1}, respectively). Among NCPC treatments, T_9 and T_{10} also recorded superior values compared to conventional treatments like T_3 (30.17 cm, 10.76 leaves and 4.98 g plant^{-1}) and T_4 (30.86 cm, 11.08 leaves and 5.33 g plant^{-1}). The SSP-applied treatment T_2 recorded lower values (28.98 cm, 9.89 leaves and 4.52 g plant^{-1}) compared to rock phosphate-based treatments, while the absolute control (T_1) showed the least values across all parameters.

At 60 DAS, T_{11} (100% P through OA-NCPF-nano RP) recorded the highest values for plant height (46.76 cm), number of leaves (20.27) and dry weight (11.75 g plant^{-1}), followed by T_{12} (45.81 cm, 19.67 leaves and 11.37 g plant^{-1}). Among RP treatments, T_9 and T_{10} also showed superior performance, whereas conventional treatments T_3 (40.18 cm, 16.37 leaves and 8.94 g plant^{-1}) and T_4 (41.55 cm, 17.11 leaves and 9.16 g plant^{-1}) recorded lower values. The SSP-applied treatment T_2 recorded significantly lower values (37.67 cm, 15.12 leaves and 8.39 g plant^{-1}) compared to rock phosphate-based treatments, while the absolute control (T_1) showed the lowest values across all parameters.

At harvest, T_{11} (100% P through OA-NCPF-nano RP) recorded the highest values for plant height (49.01 cm), number of leaves (16.84) and dry weight (13.19 g plant^{-1}), followed by T_{12} (48.45 cm, 16.25 leaves and 12.84 g plant^{-1}). Other RP treatments, such as T_9 and T_{10}, also performed better than conventional treatments like T_3 (42.69 cm, 12.44 leaves and 10.56 g plant^{-1}) and T_4 (43.72 cm, 12.98 leaves and 11.06 g plant^{-1}). The SSP-applied treatment T_2 recorded lower values (40.43 cm, 11.39 leaves and 10.36 g plant^{-1}), while the absolute control (T_1) consistently recorded the lowest values across all parameters (29.52 cm, 7.46 leaves and 6.47 g plant^{-1}).

The application of oxalic and citric acid-loaded nano clay polymer composites (NCPC) of rock phosphate or nano rock phosphate revealed that growth parameters were on par with 100% P applied through SSP and significantly enhanced maize growth parameters compared to conventional rock phosphate or direct acid-loaded rock phosphate applications. This might be due to the protection of organic acids in NCPC from microbial degradation, enhancing phosphorus solubilization. The chelating ability of oxalic and citric acids facilitated nutrient uptake (Kumar *et al*., 2018 and Kumar *et al*., 2024), while the larger surface area of nano materials improved nutrient retention (Manikandan and Subramanian, 2016 and Rashmi *et al*., 2023). These factors ensured sustained phosphorus availability, boosting metabolic processes like photosynthesis and protein synthesis, leading to improved root and shoot biomass. Nano RP applications, with their higher surface area-to-volume ratio, enhanced phosphorus bioavailability and chlorophyll biosynthesis through increased ALA (5-Amino Levulinic Acid) production, improving chlorophyll meter readings (Liu & Lal, 2014; Wu *et al*., 2019 and Beeresha & Jayadeva, 2020). Thus, organic acids-loaded NCPC with nano RP proved superior in promoting maize growth at all stages.

The application of organic acid-loaded nano clay polymer composites (NCPC) of rock phosphate significantly enhanced residual crop cowpea growth parameters, including plant height, number of leaves, branches and dry weight. Treatments T_{11} (100% P through OA-NCPF-nano RP) and T_{12} (100% P through CA-NCPF-nano RP) outperformed others by improving phosphorus (P) availability and reducing fixation. Organic acids like oxalic and citric acids in NCPCs solubilize P and chelate Fe, Al and Ca ions, minimizing fixation an sustaining P accessibility (Akande *et al*., 2010 and Jones, 1998). The nano-sized

TABLE 2

Yield parameters of maize and cowpea as influenced by organic acids loaded nano clay polymer composites of rock phosphate

Treatment	Maize				Cowpea			
	Cob length (cm)	Number of rows per cob	Kernels per row	Test weight (g 100^{-1} seeds)	Pod length (cm)	Number of pods per plant	Number of seeds per pod	Test weight (g 100^{-1} seeds)
T_1 : Absolute control	12.76	10.96	21.57	24.65	13.31	9.49	10.34	10.16
T_2 : RDF (100% P through SSP)	19.33	17.99	33.33	32.60	18.24	11.74	12.87	13.01
T_3 : RDF (100% P through RP)	14.79	14.16	25.13	25.65	20.73	11.91	13.03	13.37
T_4 : RDF (100% P through nano RP)	16.25	14.77	26.33	26.99	22.76	12.04	13.56	13.88
T_5 : 100% P through OA-RP	16.93	15.75	28.67	27.88	24.17	12.62	14.08	14.46
T_6 : 100% P through CA-RP	16.82	15.46	27.47	27.85	23.43	12.23	13.71	14.12
T_7 : 100% P through OA- nano RP	16.99	15.65	28.70	28.85	24.88	13.54	14.63	15.05
T_8 : 100% P through CA- nano RP	16.76	15.40	28.67	28.43	24.27	13.17	14.35	14.87
T_9 : 100% P through OA-NCPF- RP	17.86	16.65	30.33	30.29	25.82	14.13	15.27	15.75
T_{10} : 100% P through CA-NCPF- RP	17.59	16.57	29.73	29.46	25.39	13.96	14.89	15.22
T_{11} : 100% P through OA-NCPF- nano RP	19.05	17.47	32.47	31.79	26.58	14.87	15.92	16.48
T_{12} : 100% P through CA-NCPF- nano RP	18.80	17.38	31.77	30.92	25.96	14.35	15.48	16.06
S.Em ±	0.80	0.66	1.36	1.23	0.83	0.60	0.64	0.47
CD@5%	2.35	1.93	3.98	3.60	2.44	1.77	1.88	1.38

particles and modified clay in NCPCs ensured a slow, sustained release of nutrients, enriching the rhizosphere and promoting consistent root and shoot growth (Vikram, 2007). Conventional treatments, such as T_2 (RDF through SSP) and T_3 (RDF through RP), showed lower efficacy due to rapid P fixation (Panhwar *et al*., 2013). These results underscore the superior residual effect of NCPCs in improving cowpea growth by providing a prolonged and efficient P supply in neutral soils.

Yield Parameters

The application of organic acids-loaded nano clay polymer composites (NCPC) significantly improved maize yield parameters (Table 2). Among the treatments, T_2 (100% P through SSP) recorded the highest cob length (19.33 cm), number of rows per cob (17.99), kernels per row (33.33) and test weight (32.60 g). NCPC treatments like T_{11} (19.05 cm cob length, 17.47 rows per cob, 32.47 kernels per row, 31.79 g test weight) and T_{12} (18.80 cm, 17.38, 31.77, 30.92 g) closely followed. Treatments T_9 and T_{10} also performed better than conventional rock phosphate treatments (T_3 and T_4), while the absolute control (T_1) recorded the lowest values.

The yield parameters of residual cowpea were significantly influenced by the application of organic acids loaded nano clay polymer composites of rock phosphate (Table 2). Pod length ranged from 13.31 cm in the absolute control (T_1) to 26.58 cm in T_{11} (100% P through OA-NCPF-nano RP), with RP treatments like T_9 (25.82 cm) and T_{12} (25.96 cm) also showing notable increases. The number of pods per plant ranged from 9.49 in T_1 to 14.87 in T_{11}, with treatments T_{12} (14.35) and T_9 (14.13) also showing higher values compared to conventional treatments. The number of seeds per pod was highest in T_{11} (15.92), followed by T_{12} (15.48) and T_9 (15.27) with the absolute control showing the lowest value (10.34). Test weight also showed significant improvements, with T_{11} (16.48 g) recording the highest, followed by T_{12} (16.06 g) and T_9 (15.75 g). Conventional treatments like T_3 (13.37 g) and T_4 (13.88 g) recorded lower values, while T_2 (13.01 g) showed moderate results.

Yield of Maize-Cowpea

The kernel and stover yields of maize were significantly influenced by the application of organic acids loaded nano clay polymer composites of rock phosphate (Table 3). Among the treatments, T_2 (100% P through SSP) recorded the highest kernel yield (80.44 q ha^{-1}) and stover yield (83.47 q ha^{-1}). Organic acids loaded RP treatments, such as T_{11} (79.08 q ha^{-1} kernel yield and 82.38 q ha^{-1} stover yield) and T_{12} (79.01 q ha^{-1} kernel yield and 82.01 q ha^{-1} stover yield), closely followed. Other RP treatments, including T_9 (77.99 q ha^{-1} kernel yield, 81.23 q ha^{-1} stover yield) and T_{10} (77.38 q ha^{-1} kernel yield, 80.76 q ha^{-1} stover yield), also showed improved yields compared to conventional treatments like T_3 (57.06 q ha^{-1} kernel yield, 56.80 q ha^{-1} stover yield) and T_4 (63.29 q ha^{-1} kernel yield, 69.77 q ha^{-1} stover yield). The absolute control (T_1) recorded the lowest yields for both kernel (36.19 q ha^{-1}) and stover (38.85 q ha^{-1}).

The grain and haulm yield of residual cowpea were significantly influenced by the application of organic acids loaded nano clay polymer composites of rock phosphate (Table 3). Grain yield ranged from 775.34 kg ha^{-1} in the absolute control (T_1) to 1581.68 kg ha^{-1} in T_{11} (100% P through OA-NCPF-nano RP), with NCPC treatments like T_{12} (1563.90 kg ha^{-1}) and T_9 (1458.34 kg ha^{-1}) also showing notable increases. Haulm yield ranged from 1050.37 kg ha^{-1} in T_1 to 1963.72 kg ha^{-1} in T_{11}, with treatments T_{12} (1934.88 kg ha^{-1}) and T_9 (1906.86 kg ha^{-1}) also exhibiting higher values. Conventional treatments like T_2 (1025.90 kg ha^{-1}) and T_4 (1061.67 kg ha^{-1}) recorded moderate yields, whereas NCPC treatments significantly improved both grain and haulm yields, demonstrating their effectiveness in enhancing cowpea productivity.

The application of oxalic and citric acid-loaded nano clay polymer composites (NCPC) of rock phosphate significantly improved maize yield and yield attributes, performing at par with 100% P applied through SSP. This improvement due to enhanced growth parameters driven by the synchronized release of nutrients, including phosphorus, calcium,

TABLE 3

Yield of maize and cowpea as influenced by organic acids loaded nano clay polymer composites of rock phosphate

Treatment	Maize		Cowpea	
	Kernel yield (q ha^{-1})	Stover yield (q ha^{-1})	Grain yield (kg ha^{-1})	Haulm yield (kg ha^{-1})
T_1 : Absolute control	36.19	38.85	775.34	1050.37
T_2 : RDF (100% P through SSP)	80.44	83.47	1025.90	1272.48
T_3 : RDF (100% P through RP)	57.06	56.80	1035.01	1365.55
T_4 : RDF (100% P through nano RP)	63.29	69.77	1061.67	1471.74
T_5 : 100% P through OA-RP	68.79	75.77	1197.23	1665.93
T_6 : 100% P through CA-RP	69.06	73.69	1175.01	1643.67
T_7 : 100% P through OA- nano RP	76.20	79.38	1280.57	1808.21
T_8 : 100% P through CA- nano RP	75.84	77.88	1213.90	1777.93
T_9 : 100% P through OA-NCPF- RP	77.99	81.23	1458.34	1906.86
T_{10} : 100% P through CA-NCPF- RP	77.38	80.76	1419.45	1849.65
T_{11} : 100% P through OA-NCPF- nano RP	79.08	82.38	1581.68	1963.72
T_{12} : 100% P through CA-NCPF- nano RP	79.01	82.01	1563.90	1934.88
S.Em ±	1.15	1.10	44.19	55.13
CD@5%	3.36	3.23	129.61	161.69

magnesium, sulphur and micronutrients present in rock phosphate, sustained throughout the growing season (Fig. 1 to 3). Calcium from rock phosphate promoted meristem growth and nutrient uptake, while increased leaf numbers enhanced photo synthesis, root biomass and nutrient absorption (Rajoria *et al*., 2019). Organic acids like oxalate and citrate enhanced phosphorus solubilization, increasing soil solution phosphorus by competing with adsorbed phosphorus on soil particles (Gerke, 1992 and Jones & Darrah, 1994). Oxalic acid-loaded NCPC outperformed citric acid-loaded NCPC in boosting grain and straw yields. Studies have shown oxalic acid's superior ability to dissolve phosphorus from rock phosphate, leading to yield improvements in maize, aerobic rice and wheat (Panhwar *et al*., 2013; Wei *et al*., 2009; Roy *et al*., 2018 and Hue, 1991).

The residual effects of organic acid-loaded NCPC on cowpea yield and yield attributes significantly outperformed traditional SSP treatments, particularly in neutral soil (Table 2). Enhanced phosphorus availability, driven by organic acids like oxalic and citric acid, reduced phosphorus fixation by chelating soil minerals such as calcium, iron and aluminium, ensuring sustained nutrient supply (Hinsinger, 2001; Jones, 1998 and Roy *et al*., 2018). Nano-sized particles in NCPCs further improved nutrient adsorption and facilitated slow, controlled phosphorus release, minimizing leaching losses and providing a steady supply for crop growth (Chen *et al*., 2002; Hue *et al*., 2001 and Sarkar & Datta, 2014). Treatments such as T_{11}, T_{12}, T_9 and T_{10} demonstrated significantly higher grain and haulm yields due to these mechanisms, highlighting the superior residual effects of organic acid-loaded NCPCs in enhancing cowpea productivity, especially in phosphorus-deficient and neutral soils (Rajoria *et al*., 2019; Taalab *et al*., 2023 and Roy *et al*., 2015).

The superior growth, yield parameters and yield of maize and cowpea observed with oxalic acid-loaded NCPC of rock phosphate compared to citric acid-loaded NCPC can be attributed to oxalic acid's stronger chelating properties. It effectively solubilizes phosphorus by forming stable complexes with calcium and metal ions, enhances phosphorus availability and lowers soil pH to dissolve phosphorus-bound minerals (Liu *et al.* 2012). Oxalic acid also mobilizes nutrients like magnesium, iron and potassium, supporting essential physiological processes for biomass accumulation. Additionally, it stimulates beneficial soil microbial activity, improving nutrient cycling and availability.

The study hypothesized that organic acid like oxalic acid and citric acid would prove effective in utilizing the untapped potential of the indigenous low-grade RPs. The application of organic acids-loaded nano clay polymer composites of rock phosphate significantly improved maize and cowpea growth and yield parameters, demonstrating their potential as a sustainable alternative to conventional phosphorus fertilizers like SSP. The enhanced solubility and controlled release of phosphorus through NCPCs not only increased phosphorus use efficiency but also minimized fixation losses in soil. This innovative approach offers a viable strategy for optimizing phosphorus availability and serve as an alternative P fertilizer in the farmer's field in countries like India.

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