Supplementary Information

Sustainable Mechanochemical Activation of Rock Phosphate with Oxalic Acid for High-Efficiency Phosphorus Fertilizers

Table SI 1: XRF results. This table illustrates the chemical composition of the Eppawala Rock Phosphate (ERP) and OA-0.9 (oxalic acid modified ERP)

Component	ERP (wt% ± SE)	Oxalic acid–modified ERP (wt% ± SE)
CaO	57.9 ± 0.077	77.2 ± 0.038
P_2O_5	15.7 ± 0.014	6.84 ± 0.007
Fe_2O_3	10.7 ± 0.013	12.2 ± 0.012
SiO_2	7.53 ± 0.014	1.26 ± 0.005
Al_2O_3	3.83 ± 0.012	1.15 ± 0.006
TiO_2	1.06 ± 0.008	ND
Na_2O	1.01 ± 0.067	0.177 ± 0.038
K_2O	0.0618 ± 0.003	0.273 ± 0.002
MgO	0.184 ± 0.009	0.0317 ± 0.005
MnO	0.428 ± 0.004	0.0717 ± 0.004
SO_3	0.0809 ± 0.001	0.0123 ± 0.0003
Cl	0.366 ± 0.001	0.0199 ± 0.0001
Sr	0.505 ± 0.001	0.325 ± 0.001
Ba	0.0954 ± 0.002	0.0538 ± 0.002
Ce	0.155 ± 0.003	0.0906 ± 0.003
La	0.0753 ± 0.002	0.0399 ± 0.002
Nd	0.0637 ± 0.005	0.0327 ± 0.005
Gd	0.0569 ± 0.003	0.103 ± 0.004
Zn	0.0166 ± 0.0004	0.0140 ± 0.0005
Cu	0.0136 ± 0.0005	0.0051 ± 0.0005
Ni	0.0014 ± 0.0003	0.0054 ± 0.0003

Cd	ND	ND
Pb	0.0030 ± 0.0002	0.0034 ± 0.0002
As	0.0020 ± 0.0001	0.0014 ± 0.0001

Table SI 2: Average Crystalline size of apatite, unit cell parameters of apatite

Sample	Average crystalline size (nm)	Unit cell parameters	
		a (Å)	c (Å)
ERP	92.21	9.433	6.850
OA-0.2	72.069	9.458	6.858
OA-0.6	59.53	9.426	6.867

The average crystallite size D can be calculated from XRD peak broadening using the Scherrer equation:

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where:

- D= average crystallite size (nm)
- K= shape factor (typically 0.9)
- λ= X-ray wavelength (Cu Kα, 1.5406 Å)
- β= full width at half maximum (FWHM) of the peak (radians)
- θ= Bragg angle of the peak (degrees)

For hexagonal crystals (space group $P6_3/m$), the lattice parameters a and c can be calculated from the Bragg's law and Miller indices:

1. Bragg's Law:

$$n\lambda = 2dsin\theta$$

Where d= interplanar spacing.

2. Hexagonal system relation:

$$\frac{1}{d^2} = \frac{4}{3} \cdot \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$

Where:

- hkl= Miller indices of the diffraction plane
- a,c= lattice parameters (Å)

- d= interplanar spacing from XRD

By solving this equation for different diffraction peaks, the unit cell parameters a and c were determined.

Table SI.3: Summary of the R^2 values of all samples across all tested models

Kinetics Model	OA-0.2	OA-0.6	OA-0.9	OA-1.0	OA-1.2	Control OA	TSP
Zero Order	0.9923	0.9918	0.9300	0.9946	0.9903	0.9815	0.9901
First Order	0.9922	0.9865	0.8503	0.9276	0.9183	0.8317	0.9419
Second Order	0.9918	0.9584	0.9764	0.7804	0.8035	0.9523	0.7972
Parabolic Diffusion	0.9388	0.9121	0.9504	0.9291	0.9634	0.9860	0.9673
Elovich	0.7363	0.6476	0.8443	0.7591	0.8291	0.8748	0.8514
Power Function	0.9664	0.9121	0.9302	0.9220	0.9379	0.9844	0.9744
Higuchi	0.9388	0.8810	0.9504	0.9291	0.9634	0.9860	0.9673
Bilinear	0.9547	0.9865	0.7754	0.9555	0.9079	0.8603	0.9427
Pseudo-First Order	0.9922	0.9865	0.9819	0.8531	0.9183	0.9968	0.9419
Pseudo-Second Order	0.3409	0.020	0.7743	0.6420	0.8118	0.8632	0.8425

Figure SI.1: EDX Analysis for OA-ERP (A) OA-0.2, (B) OA-0.6, (C) OA-0.9, (D) OA-1.0 and (E) OA-1.2

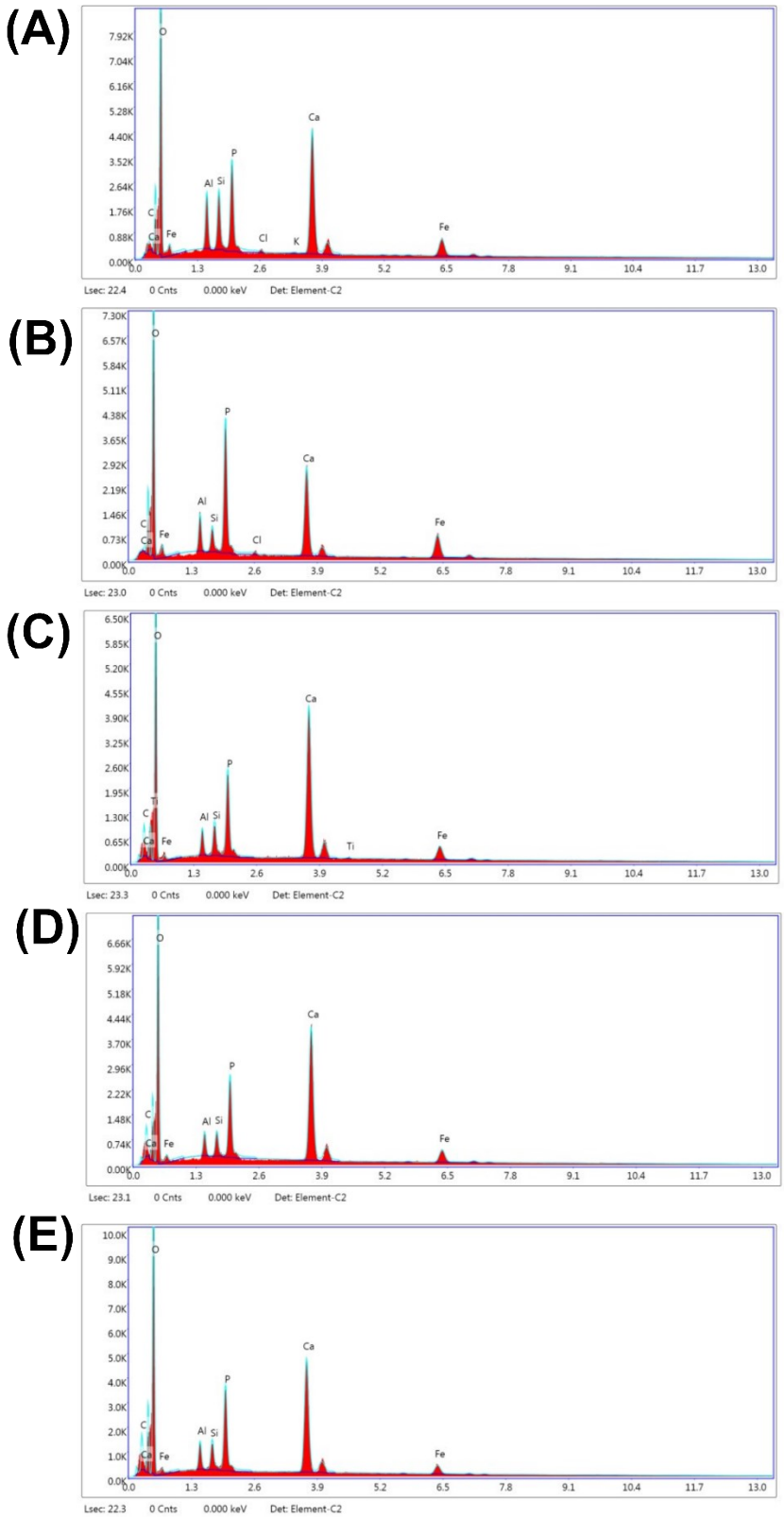

Figure SI.2: Oxalic acid release in OA-1.0 and OA-1.2

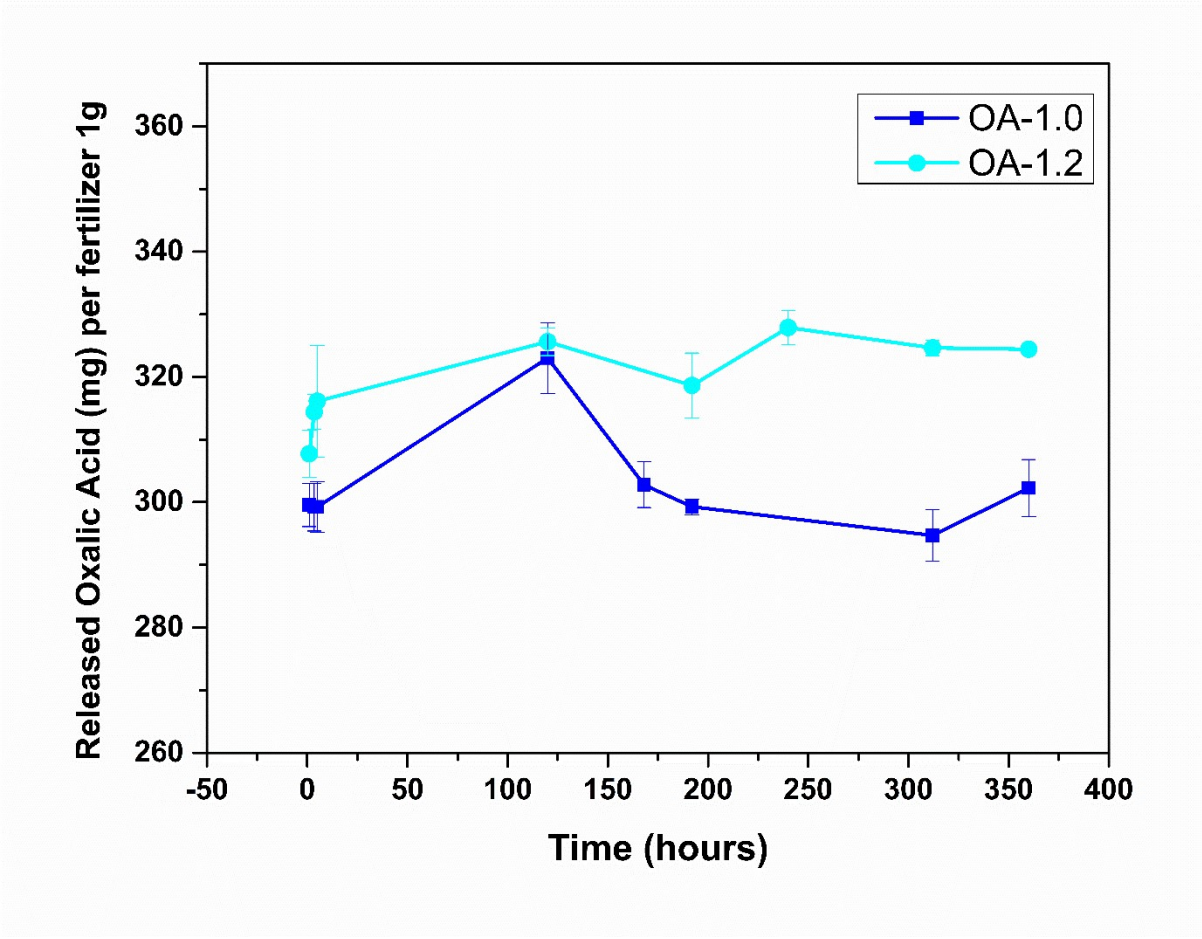

Figure SI.3: Olsen P in soil after 30 days plant bio assay

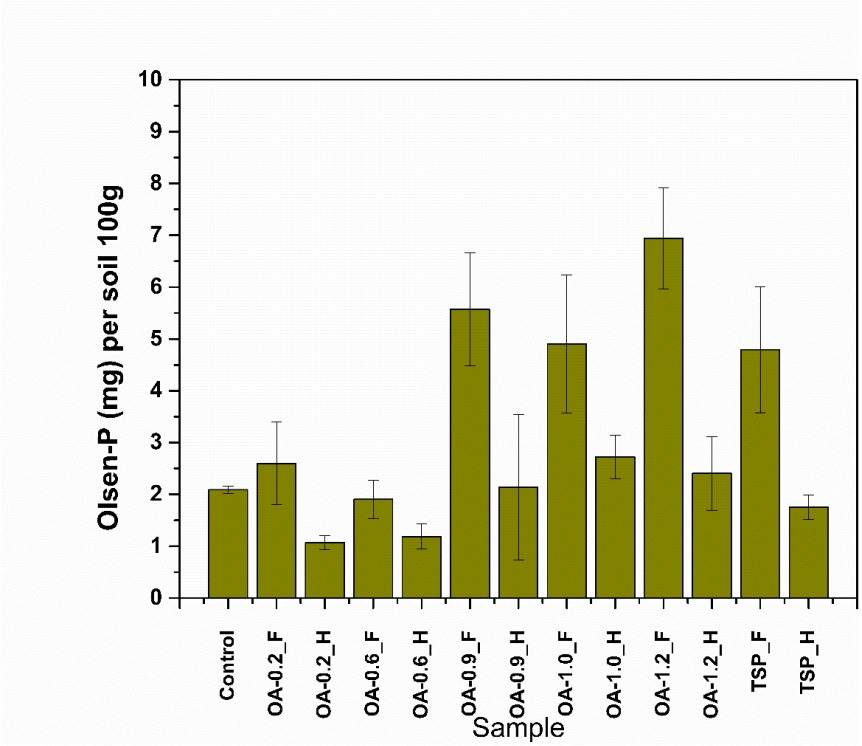

Figure SI.4: Plant trial for OA - ERP Comparing with TSP

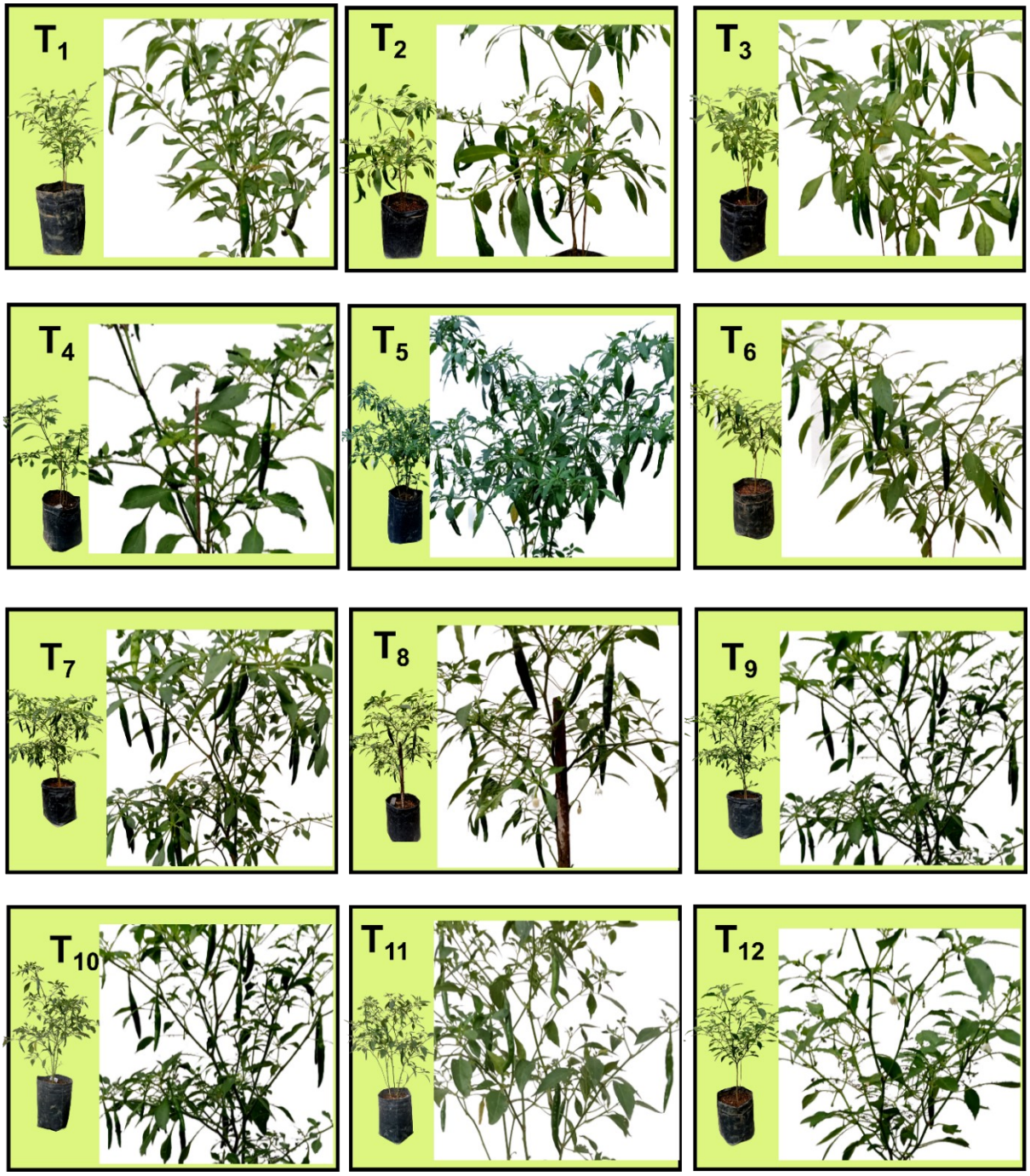

Figure SI.5: Effect of OA-ERP fertilizers on pod formation and fresh pod weight in comparison with enhanced rock phosphate (ERP) control and triple superphosphate

(TSP). (A) Number of pods per plant. (B) Fresh pod weight per plant. Different letters indicate statistically significant differences between groups (Tukey's HSD test, $p < 0.05$). (n=6)