

Green Synthesis of Phosphorous-Containing Hydroxyapatite Nanoparticles (nHAP) as a Novel Nano-Fertilizer: Preliminary Assessment on Pomegranate (*Punica granatum* L.)

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Table S1. GC/ MS results of the ethanolic extract of *Punica granatum* leaves under study: RT (retention time); MW (molecular weight); MF (molecular formula).

Treatment	RT	MW	MF	AREA%	Probabilities of the Detected Compounds
Control	5.18	355	C ₂₂ H ₁₃ NO ₄	5.43	4-Hydroxy-3-(2-oxo-2H-1-oxa-3-phenanthryl)-2(1H)-quinolinone
	11.90	436	C ₃₁ H ₆₄	1.03	Hentriacontane (CAS)
	18.24	254	C ₁₈ H ₃₈	1.11	Octadecane (CAS)
	21.17	126	C ₈ H ₁₄ O	1.21	1-Octen-3-one (CAS)
	24.24	828	C ₄₂ H ₇₀ O ₅ Yb	57.44	bis(2,6-di-t-butyl-4 methylphenoxo)ytterbium(II)
	24.39	206	C ₁₆ H ₁₄	2.16	trans, trans-1,4-Diphenyl-1,3-butadiene
	25.94	224	Cl ₆ H ₃₂	1.54	7-Hexadecene, (Z)-
	27.77	218	C ₁₅ H ₂₂ O	1.95	aR-Turmerone
	28.28	254	C ₁₈ H ₃₈	1.75	Hexadecane, 7,9-dimethyl (CAS)
	30.23	414	C ₂₀ H ₄₁ Cl ₃ Si	1.24	Silane, trichloroicosyl-
	30.36	212	C ₁₅ H ₃₂	1.20	Pentadecane (CAS)
	32.34	212	C ₁₅ H ₃₂	3.00	Dodecane, 2,6,11-trimethyl-
	32.95	298	C ₁₉ H ₃₈ O ₂	1.67	Octadecanoic acid, methyl ester (CAS)
	34.23	172	C ₁₁ H ₂₄ O	2.05	Ether, hexyl pentyl (CAS)
	36.07	294	C ₁₉ H ₃₄ O ₂	4.94	9,12-Octadecadienoic acid (Z, Z)-, methyl ester
	36.17	296	C ₁₉ H ₃₆ O ₂	3.19	9-Octadecenoic acid, methyl ester, (E)-
	37.78	635	C ₁₈ H ₁₀ Br ₅ N	1.48	Tris(2,4-dibromophenyl) amine
	39.11	404	C ₂₀ H ₃₆ O ₈	2.22	Tributyl 2-acetylcitrate
	39.45	310	C ₂₂ H ₄₆	1.31	Docosane (CAS)
	41.16	370	C ₂₂ H ₄₂ O ₄	4.10	Hexanedioic acid, bis(2-ethylhexyl) ester (CAS)

Table S1. Continued.

Treatment	RT	MW	MF	AREA%	Probabilities of the Detected Compounds
NPK	5.19	72	C ₄ H ₆ D ₂ O	12.97	Methyl 1-Dideuterio-2-propenyl ether
	5.27	646	C ₃₆ H ₅₄ O ₁₀	9.32	Tetra-tert-butyl 2,6-di(3-propenyl)-3,7-dim ethoxybicyclo [3.3.0] octa-3,7-diene-2,4,6,8-di

carboxylate				
5.39	638	C ₃₆ H ₆₆ Si ₅	6.52	1,2-Bis(t-tributylsilyl)-1,2-diphenylcyclotrisilane
5.70	640	C ₃₆ H ₃₇ BrO ₄ Si	1.82	15-Bromo-4,4'-bis(t-butyl)-11,12-diethylnaphtho[12-f]phenanthrol[2,1-d]-(1,3,2)-dioxasilepine-10,13-dione
6.07	648	C ₄₄ H ₃₂ N ₄ O ₂	1.36	meso-Tetraphenyl-2,3-cis- dihydroxy-2,3-chlorin
10.14	578	C ₂₀ H ₂₂ Br ₄	1.26	2,2',5,5'-Tetrabromo-4,4'- di-tert-butyl bi phenyl
24.23	220	C ₁₅ H ₁₂ N ₂	36.33	2,3-dicyano-7,7-di methyl-5,6-benzonorbornadiene
31.18	278	C ₂₀ H ₃₈	2.64	3-Eicosyne
32.36	671	C ₃₂ H ₅₇ NO ₆ Sn	2.34	tert-Butyl 3-Tributylstannyl-4- (methoxy ethoxy) -N-(tert-butoxy carbonyl) tyrosine
32.96	270	C ₁₇ H ₃₄ O ₂	2.70	Hexadecanoic acid, methyl ester (CAS)
36.08	288	C ₁₅ H ₂₈ O ₃ S	5.45	Undec-10-enyl But-3-enesulfonate
36.18	296	C ₁₉ H ₃₆ O ₂	3.97	9-Octadecenoic acid methyl ester (CAS)
41.17	370	C ₂₂ H ₄₂ O ₄	1.66	Hexanedioic acid, bis(2-Ethylhexyl) ester (CAS)
42.59	394	C ₂₈ H ₅₈	1.51	Octacosane (CAS)
43.51	592	C ₃₆ H ₃₂ O ₈	1.57	1,5-bis[(6-methoxyphenyl) methyl-1,3-benzodioxol-3,9-Dioxo-2,4,8,10-tetrao xa-3,9-dithiaspiro [5.5] undecane
45.54	228	C ₅ H ₈ O ₆ S ₂	2.51	{4-[2'-(2''-(4'''-<Methoxycarbonyl>-2''',3'''-dichloro phenyl)-3''-ethyl-5''-pyrrolyl] methyl] butyryl]-2,3-di chlorophenoxy]-acetic acid
46.60	615	C ₂₇ H ₂₅ C ₁₄ NO ₇	1.55	3-Pentanol, 2,4-dimethyl-
46.77	116	C ₇ H ₁₆ O	1.37	2,4,6,8-Tetramethyl-1-undecene
46.90	210	C ₁₅ H ₃₀	1.77	Diethyl 5-[(isopropoxy)carbonyl]-5-methyl-2-phenylte tra hydro-1 <i>H</i> -pyrrol-3yl} phosphonate
54.13	383	C ₁₉ H ₃₀ NO ₅ P	1.37	

Treatment	RT	MW	MF	AREA%	Probabilities of the Detected Compounds
nHAP_PPE 50	5.14	620	C ₂₃ H ₂₈ Br ₄	7.22	1,7-Bis (3,5-bis (bromomethyl)phenyl) heptane
	5.20	40	Ar	6.76	Argon (CAS)
	5.33	116	C ₅ H ₈ O ₃	8.25	4,5-Dimethyl-1,3-dioxolan-2-one
	5.40	651	C ₃₉ H ₄₉ N ₅ O ₄	4.08	ẽ-meso-di methylamino methyl-porphyrin
	5.48	40	C ₃ H ₄	4.97	1,2-Propadiene (CAS)
	5.56	660	C ₃₆ H ₄₄ FN ₄ NbO	1.95	Fluoro(2,3,7,8,12,13,17,1 8-octaethylporphyrinato)oxoniobium
	5.82	543	C ₃₁ H ₃₀ ClN ₃ O ₄	1.66	C-CAM-3-cyanomethyl Ether
	7.25	660	C ₂₉ H ₂₆ Br ₂ O ₈	1.53	3',5'-Dimethoxyphenyl 1,8-Dibomo-4,5-diisoprop oxyanthraquinone-2-carboxylate
	8.00	84	CH ₂ Cl ₂	2.09	Methane, dichloro- (CAS)
	10.98	630	C ₄₂ H ₃₁ ClN ₂ O ₂	2.05	1-methyl-2,2-diphenyl-3-oxo-6-chloro-5-(5')- (1'-methyl-2',2'-diphenyl-3'-oxol1'-benzazoly) -1-benzazole
	24.24	220	C ₁₅ H ₂₄ O	37.29	Butylated Hydroxytoluene
	31.18	278	C ₂₀ H ₃₈	6.18	Neophytadiene
	32.35	212	C ₁₅ H ₃₂	1.55	Pentadecane (CAS)
	36.08	294	C ₁₉ H ₃₄ O ₂	1.61	9,12-Octadecadienoic acid, methyl ester, (E,E)- (CAS)
	36.18	296	C ₁₉ H ₃₆ O ₂	1.83	9-Octadecenoic acid (Z)-, methyl ester (CAS)
	41.16	196	C ₁₃ H ₂₄ O	2.08	Cyclobutanone, 2-(2,6-dimethylheptyl)-
	42.59	603	C ₃₈ H ₃₂ ClF ₂ N ₃	2.75	4-(4-Chlorophenyl)-2-(2- phenylethyl)-6-[4- [bis

				(4-fluorophenyl) methyl] piperazinyl-1-yl]benzonitrile
51.83	731	C ₃₉ H ₅₇ NO ₃ Ti ₃	1.86	[Tri {Titanium-penta methyl cyclopentadienyl(ac-oxa)}(ac-methyl){N-(2,6-dimethyl phenyl)}]
51.92	597	C ₃₂ H ₃₉ NO ₁₀	2.72	3-Pyridinecarboxylic acid 2,7,10-tris(acetyloxy)-1,1a,2,3,4,6,7,10,11,11a-decahydro-1,1,3,6,9-pentamethyl-4-oxo-4a,7a-epoxy-5H-cyclopenta[a]cyclopropa[f]cycloundecen-11-yl ester
52.61	584	C ₃₄ H ₆₈ O ₅ Si	1.55	Glycerine-1,3-dimyristate, 2-O-trimethylsilyl-

Table S1. Continued.

Treatment	RT	MW	MF	AREA %	Probabilities of the Detected Compounds
nHAP_PPE1000	5.26	170	C ₅ H ₈ Cl ₂ O ₂	28.66	3,3-Dichloro-5-hydroxy-2-methyltetrahydrofuran
	5.86	646	C ₃₉ H ₄₈ N ₄ NiO	1.46	Nickel(II) η -meso-(2-Formylvinyl)octaethylchlorin
	11.36	632	C ₂₅ H ₁₆ Br ₄	1.76	4,4',4'',4'''-Tetra bromo tetra phenylmethane
	21.72	601	C ₃₁ H ₂₁ ClFN ₃ O ₃ S ₂	1.14	7-{4'-[4''-(5'''-Chloro-2'''-methoxybenzoyl)amino]phenyl}-2-(thienylmethylenenyl)-2-(thienylmethylenel)-2,3-dihydro-5H-thiazolo[3,2-a]pyrimidine
	24.23	828	C ₄₂ H ₇₀ O ₅ Yb	45.15	bis(2,6-di- <i>t</i> -butyl-4-methylphenolato)tris(tetrahydrofuran)ytterbium(II)
	31.18	196	C ₁₂ H ₂₀ O ₂	1.67	(1 <i>RS</i> ,5 <i>SR</i> ,6 <i>SR</i>)-6-Pentyl-2-oxabicyclo[3.3.0]octan-3-one
	32.35	184	C ₁₃ H ₂₈	1.18	Decane, 2,6,8-trimethyl- (CAS)
	36.08	138	C ₁₀ H ₁₈	1.52	cis-Pinane
	40.40	478	C ₅₂ H ₆₀ O ₄	1.21	26,28-Dihydroxy-25,27-dioxaocta-4-ene-2,6-diynyl- <i>p</i> -tert-butylcalix[4]arene
	41.16	370	C ₂₂ H ₄₂ O ₄	2.18	Hexanedioic acid, dioctylester (CAS)
	42.60	635	C ₁₈ H ₁₀ Br ₅ N	1.33	(4-Bromophenyl)bis(2,4-dibromophenyl)amine
	48.02	628	C ₂₈ H ₃₈ Br ₂ S ₃	2.46	5,5''-Dibromo-3,3'',4,4''-tetra-butyl-2,2':5',2''-terthiophene
	48.62	615	C ₂₇ H ₂₅ Cl ₄ NO ₇	1.22	{4-[2'-[2''-(4'''-<Methoxycarbonyl>-2'''',3'''-dichlorophenyl)-3''-ethyl-5''-pyrrolyl]methyl]butyryl]-2,3-dichlorophenoxy]-acetic acid
	49.90	648	C ₃₅ H ₃₈ Cl ₂ N ₄ O ₄	1.36	2,4-bis(4-chloroethyl)-6,7-bis[4-methoxycarbonyl]ethyl]-1,3,5-trimethylporphyrin
	50.24	599	C ₃₆ H ₄₄ N ₄ OV	1.19	Vanadyl octaethylporphyrin
	50.36	658	C ₄₂ H ₅₈ O ₆	1.42	Fucosanthin
	51.06	596	C ₄₀ H ₅₂ O ₄	1.17	Astaxanthin
	52.14	490	C ₃₃ H ₃₈ N ₄	1.51	13,17-Diethyl-2,8,12,18-tetramethyl-3,5-(2,2-dimethylpropano)porphyrin
	52.95	713	C ₃₈ H ₄₃ N ₅ O ₅ Zn	1.29	{[3 <i>Z</i>]-2-[(Dimethylcarbamoyl)methyl]-3-ethylidene-13,17-bis[2'-(methoxycarbonyl)ethyl]-2,7,12,18-tetramethyl-2,3-dihydroporphytinato]} zinc (II)
	53.87	628	C ₂₈ H ₃₈ Br ₂ S ₃	1.13	5,5''-Di bromo-3,3'',4,4''-tetra butyl-2,2':5',2''-terthiophene

Table S1. Continued.

Treatment	RT	MW	MF	AREA%	Probabilities of the Detected Compounds
nHAP_CE50	5.11	177	C ₇ H ₁₅ NS ₂	0.98	5,6-dihydro-2-ethyl-4,6-dimethyl-4 <i>H</i> -1,3,5-dithiazimethyl-4 <i>H</i> -1,3,5-dithiazine
	5.18	130	C ₈ H ₁₈ O	1.62	2-Hexanol, 2,3-dimethyl-(CAS)
	21.36	366	C ₂₆ H ₅₄	0.53	Hexacosane (CAS)
	23.79	156	C ₁₁ H ₂₄	0.73	Undecane (CAS)
	24.24	246	C ₁₄ H ₁₈ N ₂ O ₂	9.01	1-(4-Methoxyphenyl)-2-pentene-1,4-dione-4-dimethylhydrazone
	26.09	212	C ₁₅ H ₃₂	0.85	Pentadecane
	28.28	170	C ₁₂ H ₂₆	1.63	Undecane, 2-methyl- (CAS)
	30.36	226	C ₁₆ H ₃₄	1.22	2,6,10 - trimethyl - tridecane (WITHOUT stereochemistry)
	31.19	610	C ₂₆ H ₁₆ C ₁₄ O ₅ P ₂	0.66	1,8-di (dichloro-phosphiny lidenoxy)-9,9-diphenyl-1-anthrone
	32.35	296	C ₂₁ H ₄₄	1.79	Heptadecane, 2,6,10,15-tetramethyl-(CAS)
	32.95	270	C ₁₇ H ₃₄ O ₂	12.07	Hexadecanoic acid, methyl ester (CAS)
	34.24	296	C ₂₁ H ₄₄	1.57	Heptadecane, 2,6,10,15-tetramethyl-(CAS)
	36.09	294	C ₁₉ H ₃₄ O ₂	35.77	9,12-Octadecadienoic acid, methyl ester
	36.18	296	C ₁₉ H ₃₆ O ₂	24.25	9-Octadecenoic acid, methyl ester
	36.63	298	C ₁₉ H ₃₈ O ₂	3.97	Octadecanoic acid methyl ester (CAS)
	37.79	310	C ₂₂ H ₄₆	0.88	Docosane (CAS)
	39.46	618	C ₄₄ H ₉₀	0.69	Tetratetracontane (CAS)
	45.51	128	C ₉ H ₂₀	0.54	Hexane, 2,4,4-trimethyl-Ethyl5,6-Diphenyl
	48.23	579	C ₃₇ H ₃₀ N ₃ O ₂ P	0.63	-3-(triphenyl lphosphoranylideneamino) pyridazine-4-carboxylate
	54.18	83	C ₄ H ₅ NO	0.61	Isoxazole, 5-methyl-(CAS)

Table S1. Continued.

Treatment	RT	MW	MF	AREA%	Probabilities of the Detected Compounds
nHAP_CE1000	5.14	130	C ₇ H ₁₄ O ₂	6.11	Pentanoic acid, 3-methyl-, methyl ester
	5.26	137	C ₈ H ₁₁ NO	11.53	7-hydroxy-5,6,7,8-tetra hydroindolizine
	5.33	74	C ₄ H ₁₀ O	6.89	Ethane, 1,1'-oxybis-
	5.40	612	C ₄₀ H ₄₄ N ₄ O ₂	11.30	4,16-Di-t-butyl-10,11,22,23-tetramethyl-1,8,13,20-tetraazatetrabenzo[c,d,h: m:r]cyclooctadeca-hexadecaene-6,18-diol
	5.56	606	C ₃₈ H ₄₆ N ₄ O ₃	9.14	Methyl 5-ethyl-5- dimethyl-delta-methyl Mesopyrophaeophorbide A and homologues
	5.84	644	C ₄₁ H ₄₀ O ₇	1.30	5''-(1,1-Dimethylethyl) -2 2',2'',2''',2''''-penta methoxy [1,1':3',1'':3'',1''':3''''.1''-quinquephenyl] -3,3''''-dicarboxyaldehyde
	17.64	628	C ₂₈ H ₃₈ Br ₂ S ₃	1.49	5,5''-Dibromo-3,3'',4,4''-tetrabutyl-2,2':5',2''-terthiophene
	21.59	618	C ₁₆ H ₅₀ BF ₃ N ₆ Si ₈	1.28	Fluorobis [3-fluorodimethylsilyl-2,2,4,4,6,6-hexa methyl-1,3,5-triaza-2,4,6-trisilacyclohexyl] borane
	23.16	1036	C ₆₇ H ₄₈ N ₄ O ₄ Zn	1.45	(R, S)-{5-[4(e)-(2-(1,4,5,8,9,10-Hexahydro-1,4,5,8-tetraoxo-9,10-(o-benzeno) anthracenyl) cyclohex-(e)-yl l] -10,15,20-tri-p-tolyl porphyrinato} zinc (II)
	24.23	828	C ₄₂ H ₇₀ O ₅ Yb	34.65	bis(2,6-di-t-butyl-4-methylphenolato) tris(tetrahydrofuran)ytterbium (II)
	24.38	609	C ₃₇ H ₄₇ N ₅ O ₃	1.42	5-methoxy-15-nitro-2,3,7,8,12,13,17,18-octaethylporphyrin
	24.83	748	C ₅₂ H ₆₀ O ₄	1.45	26,28-Dihydroxy-25,27-dioxaocta-4-ene-2,6-diynyl-p-tert-butylcalix [4] arene
	26.28	726	C ₂₁ H ₂₇ Mo ₂ O ₆ P ₅	1.29	Mo (CO) ₂ [(C ₄ H ₉ -C-P) P ₂] Mo (CO) ₄ [(C ₄ H ₉ -C-P) ₂]

31.18	156	$C_{10}H_{20}O$	1.26	(2,4,6-Trimethylcyclohexyl) methanol
32.34	170	$C_{11}H_{22}O$	1.28	Octyl Allyl Ether
36.63	632	$C_{25}H_{16}Br_4$	1.28	4,4',4'',4'''-Tetrabromotetraphenylmethane
41.16	370	$C_{22}H_{42}O_4$	1.91	Hexanedioic acid, dioctyl ester (CAS)
44.08	621	$C_{27}H_{34}BrCdN_5$	1.93	Cadmium bromide hepta methylnitrite porphine complex
52.04	640	$C_{16}H_4Br_4S_4$	1.39	2,7,12,17-tetrabrom-(all-às) cyclotetrathiophen (2,7,12,17-tetrabrom Cyclo octa[1,2-b:4,3-b':5,6-b'':8,7-b''']tetrathiophen

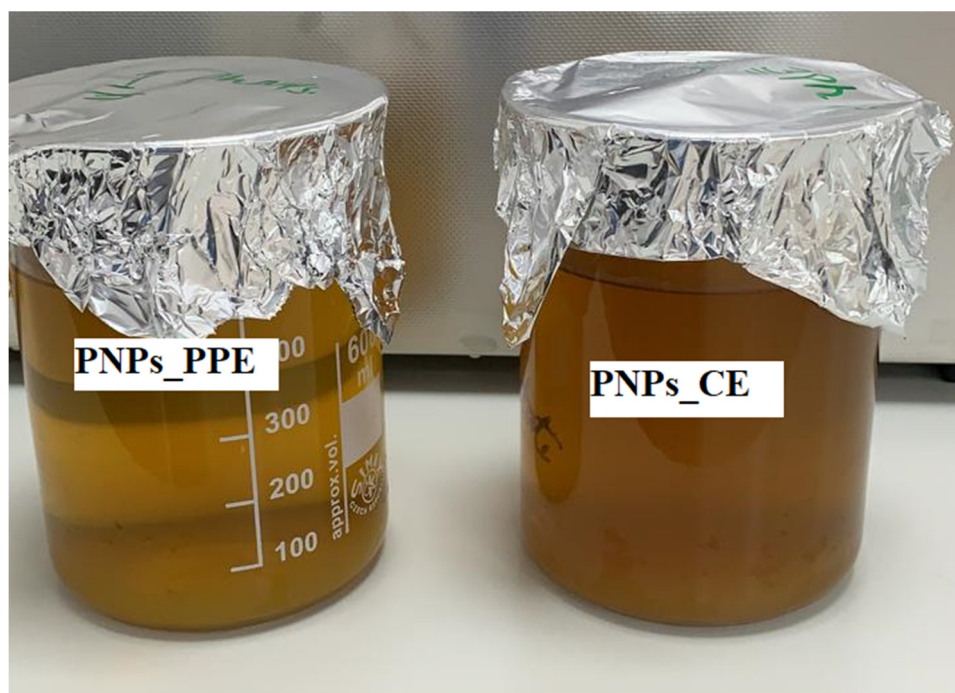


Figure S1. Preparation of phosphorous nanoparticles biologically using pomegranate peel extract (nHAPs_PPE) and coffee ground extract (nHAPs_CE).

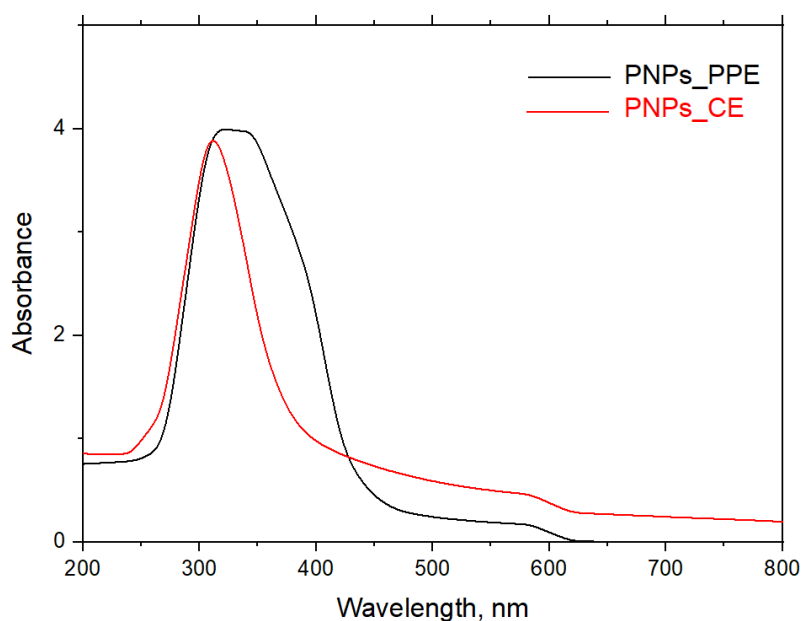


Figure S2. UV-Visible spectral analysis of green synthesized nHAPs_PPE and nHAPs_CE.