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Pre-emergence herbicidal efficiency and uptake of atrazine-loaded zein nanoparticles: a sustainable alternative to weed control

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SUPPLEMENTARY MATERIAL

Table S1 The concentration of salts presents in the nutrient solution.

Salt	Concentration
KH_2PO_4	1 mM
$Ca(NO_3)_2.4H_2O$	4 mM
K_2SO_4	2 mM
$(NH_4)_2SO_4$	4 mM
$MgSO_4.7H_2O$	2 mM
H_3BO_3	92.5 µM
$MnCl_2.4H_2O$	18 µM
$ZnCl_2$	1.5 µM
$Na_2MoO_4.2H_2O$	0.56 µM
$CuCl_2.2H_2O$	0.66 µM
$FeSO_4$	100 µM

Table S2 Physico-chemical properties of soil.

Parameters	Medium clay soil[a]
Total sandy ($g.kg^{-1}$)	691
Silt ($g.kg^{-1}$)	48
Clay ($g.kg^{-1}$)	261
pH ($CaCl_2$)	5.3
OM ($g.dm^{-3}$)	67
P ($mg.dm^{-3}$)	77
K ($mmolc.dm^{-3}$)	10.6
Ca ($mmolc.dm^{-3}$)	41
Mg ($mmolc.dm^{-3}$)	20
H+Al ($mmolc.dm^{-3}$)	28
SB ($mmolc.dm^{-3}$)	71.6
CEC ($mmolc.dm^{-3}$)	99.6
V (%)	72

[a]Soil analyzed at the Laboratory of Mineral Fertilizers of the Superior School of Agriculture "Luiz de Queiroz", University of São Paulo, Piracicaba, São Paulo, Brazil. OM: organic matter; H+Al: acidity potential; SB: sum of exchangeable bases; CEC: cation exchange capacity; V: base saturation.

Table S3 Atrazine contents in roots stems and leaves of (c) *Bidens pilosa* and (d) *Zea mays* subjected to treatment with zein nanoparticles containing the herbicide (ZNP-ATZ) and commercial herbicide (ATZ). Values are represented by the mean ± SD (n=3), with exposure times to each treatment of 2, 4, 8, 12, 24, 36, and 48 h. Different letters indicate that the values were significantly different according to the Tukey test ($p < 0.05$). Lowercase letters compare values as a function of exposure time and uppercase letters compare values between treatments.

Exposure time (h)	Atrazine quantification (μg g^{-1})					
	Root		Stem		Leaf	
	ATZ	ZNP-ATZ	ATZ	ZNP-ATZ	ATZ	ZNP-ATZ
2	32.65 ± 0.60 ^{aBC}	16.24 ± 3.16 ^{aA}	1.31 ± 1.12 ^{aA}	1.83 ± 1.19 ^{aA}	0 ^{aA}	0 ^{aA}
4	25.98 ± 4.63 ^{aB}	25.82 ± 3.90 ^{bB}	2.60 ± 0.81 ^{aA}	3.68 ± 0.81 ^{abAB}	0.15 ± 0.25 ^{aA}	0.32 ± 0.56 ^{aA}
8	35.64 ± 7.91 ^{aBC}	29.07 ± 5.53 ^{bcB}	6.33 ± 0.52 ^{bBCD}	6.38 ± 1.91 ^{bcBC}	0.80 ± 0.77 ^{aA}	0.49 ± 0.28 ^{aA}
12	29.56 ± 4.25 ^{aBC}	31.04 ± 5.35 ^{bcB}	6.43 ± 0.54 ^{bCD}	7.02 ± 0.54 ^{cdC}	1.60 ± 1.49 ^{aA}	6.95 ± 1.62 ^{bB}
24	30.46 ± 4.28 ^{aBC}	35.28 ± 4.95 ^{bcB}	6.63 ± 0.81 ^{bCD}	8.80 ± 1.25 ^{dD}	8.43 ± 1.33 ^{bB}	10.97 ± 1.57 ^{bB}
36	29.17 ± 5.78 ^{aBC}	36.03 ± 5.58 ^{bcB}	5.61 ± 0.44 b^{BC}	5.60 ± 0.18 ^{bcC}	18.96 ± 0.49 ^{cC}	11.35 ± 4.30 ^{bB}
48	32.66 ± 4.65 ^{aBC}	43.56 ± 4.49 ^{cC}	5.63 ± 0.60 b^{BC}	5.65 ± 0.38 ^{bcC}	28.06 ± 2.97 ^{dD}	19.16 ± 0.97 ^{cC}

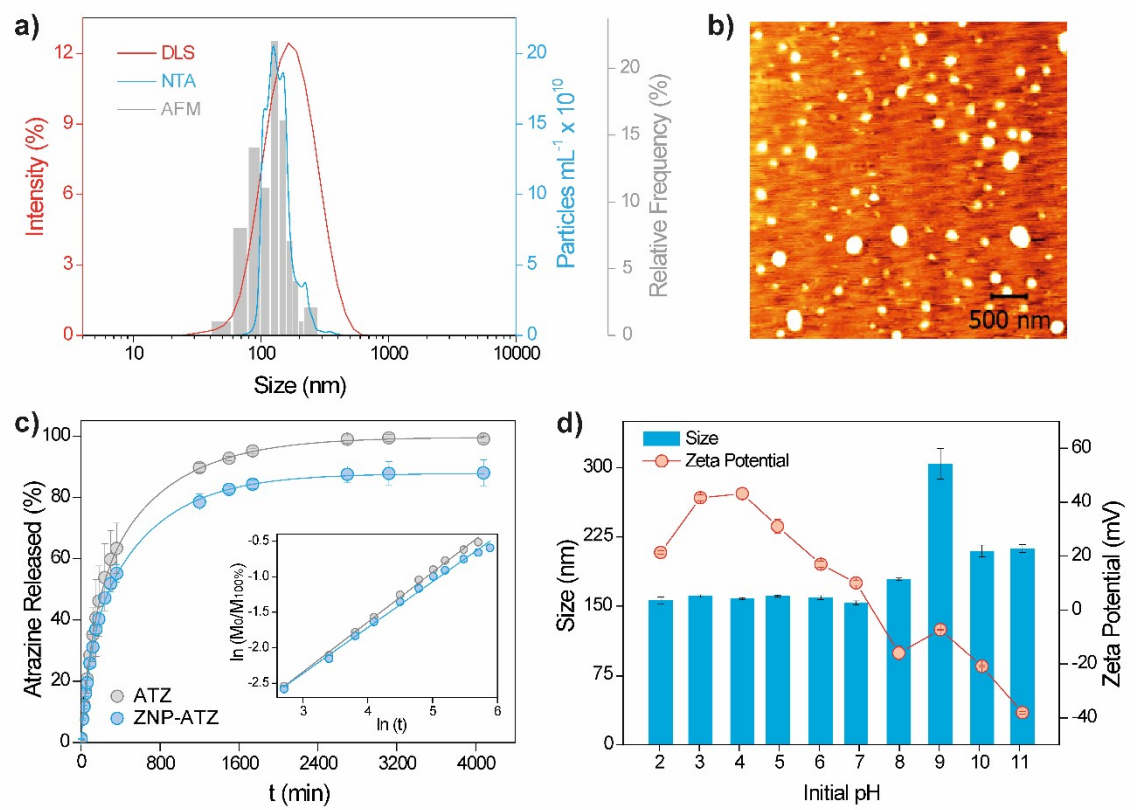

Fig. S1 Characterization of zein nanoparticles with atrazine (ZNP-ATZ). (a) Size distribution by DLS, NTA, and AFM techniques; (b) AFM micrograph of ZNP-ATZ nanoparticles; (c) *In vitro* release profile of commercial atrazine (ATZ) and encapsulated in zein nanoparticles, followed by adjustment of release kinetics for ATZ and ZNP-ATZ to the mathematical model of Korsmeyer-Peppas; (d) Hydrodynamic size and zeta potential of nanoparticles as a function of pH.

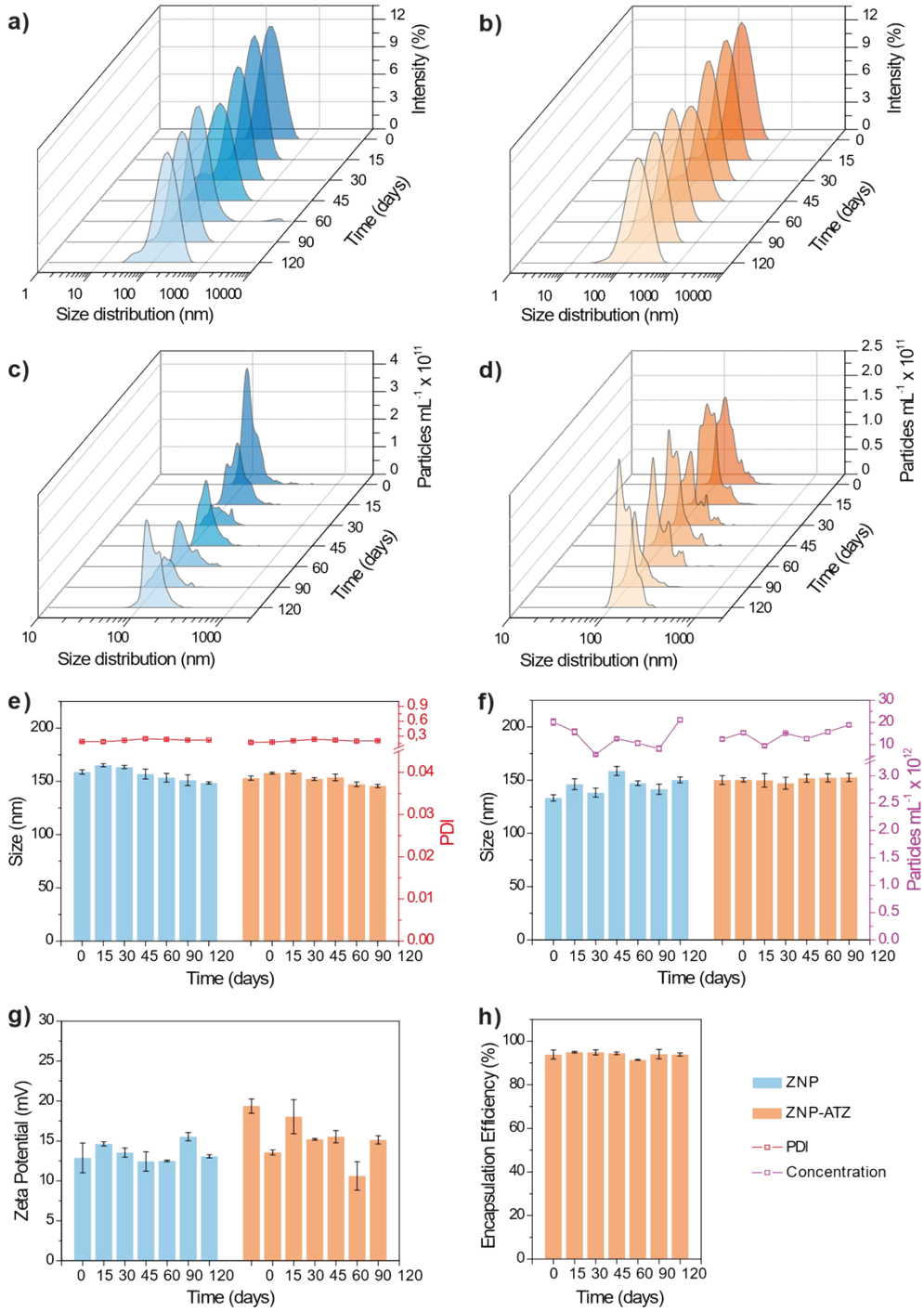

Fig. S2 Characterization and stability of zein nanoformulations on days 0, 15, 30, 45, 60, 90, and 120 days after preparation, performed at 25 °C (n=3). Distribution of the hydrodynamic diameter of (a) zein nanoparticles (ZNP) and (b) zein nanoparticles with atrazine (ZNP-ATZ) obtained by DLS. Size distribution of (c) ZNP and (d) ZNP-ATZ nanoparticles obtained by NTA. (e) average hydrodynamic size and polydispersity index of ZNP and ZNP-ATZ nanoparticles. (f) average size and concentration of ZNP and ZNP-ATZ nanoparticles, obtained by NTA. (g) zeta potential of ZNP and ZNP-ATZ nanoparticles. (h) encapsulation efficiency of atrazine in zein nanoparticles.

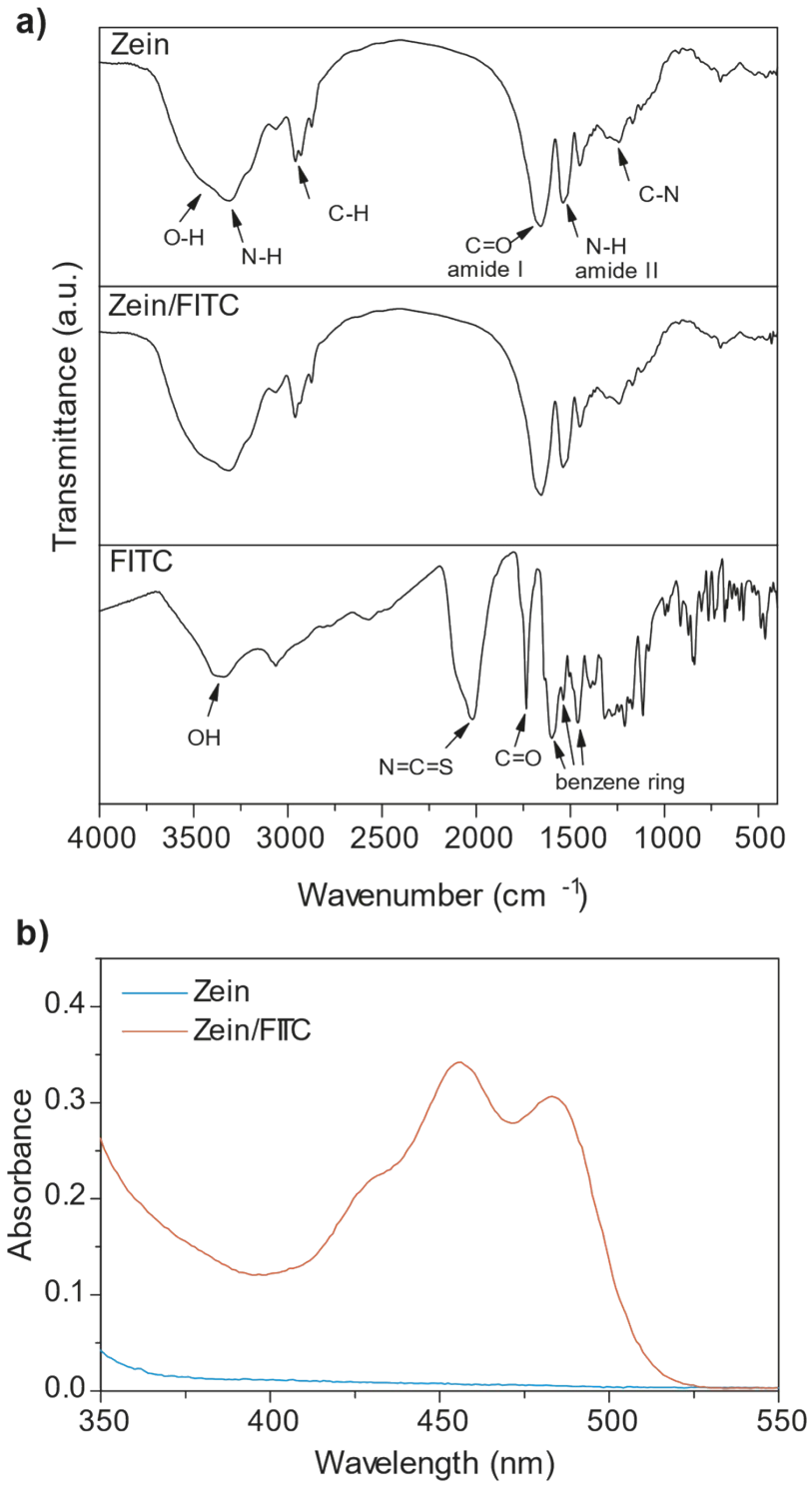

Fig. S3 (a) Infrared spectra for zein, fluorescein isothiocyanate (FITC), and FITC-labeled zein. (b) Absorption curves in the visible region for zein and FITC-labeled zein solution.

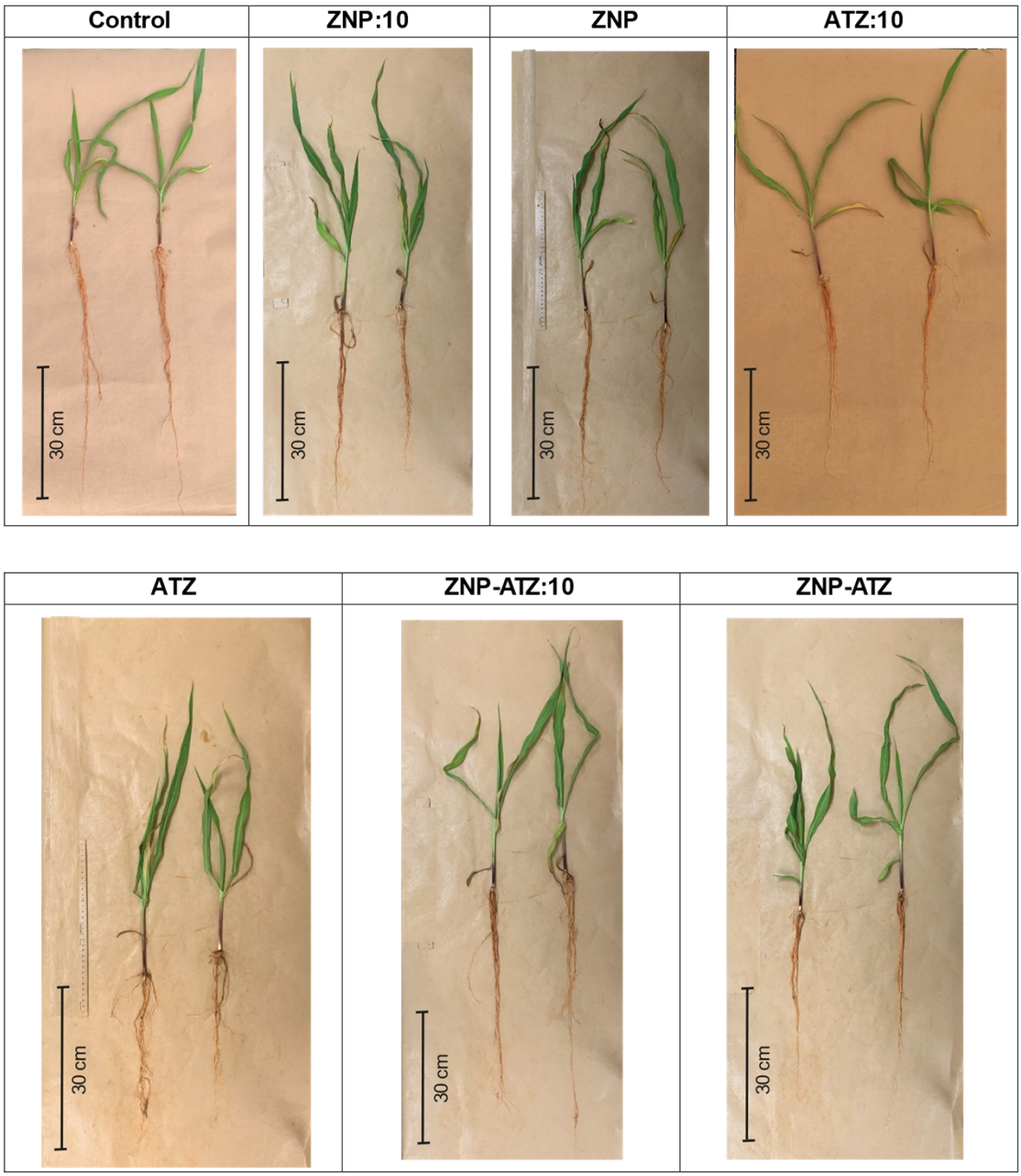

Fig. S4 Visual symptoms in *Zea mays* plants from the pre-emergence experiment were submitted to the following treatments: control, nanoparticles without atrazine (ZNP), commercial atrazine (ATZ), and nanoparticles with atrazine (ZNP-ATZ) at doses of 2000 g ha^{-1} and 200 g ha^{-1} (indication of :10).