Degradation Of Bis-*p*-Nitrophenyl Phosphate Using Zero-Valent Iron Nanoparticles

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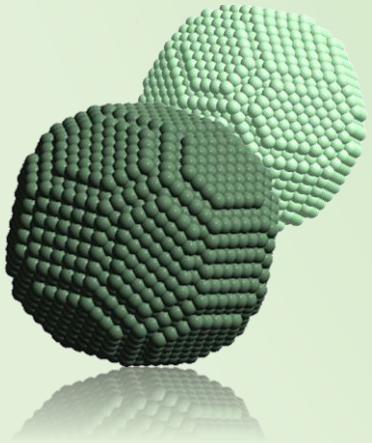


Nanosafe 2016
Grenoble, 10th November

Hydrolysis of phosphodiester bonds has been of much interest for both chemists and for biochemists

Why?

Biochemists

these are related to:

- Driving and storing information on genetic materials, for example: DNA and RNA
- Energy transfer
- Phosphorylation protein
- Many intermediaries metabolites
- Inhibiting the action of acetylcholinesterase (AChE) in nerve cells

Chemists

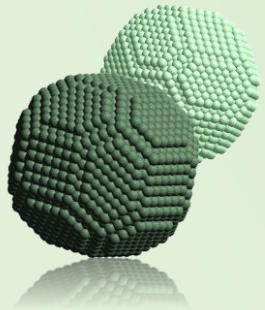
these are widely used like:

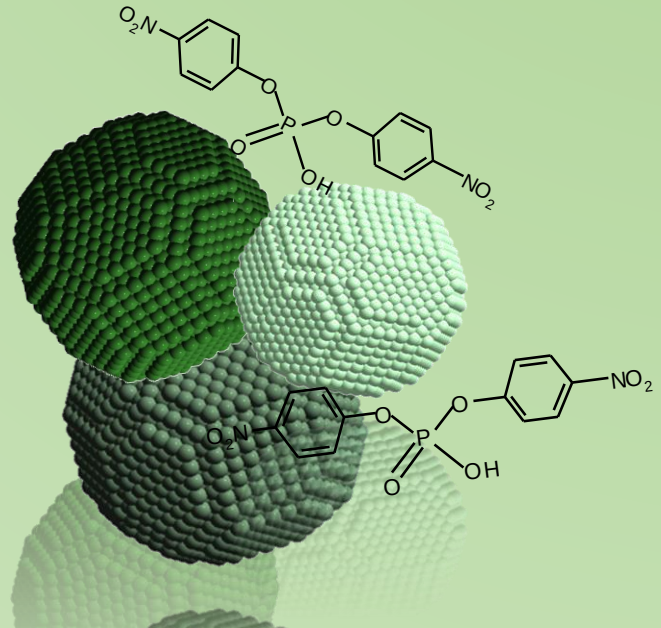
- Agrochemical

  ✓ In the formulation of insecticides and herbicides which are washed by rains into the groundwater and some is absorbed in plants.

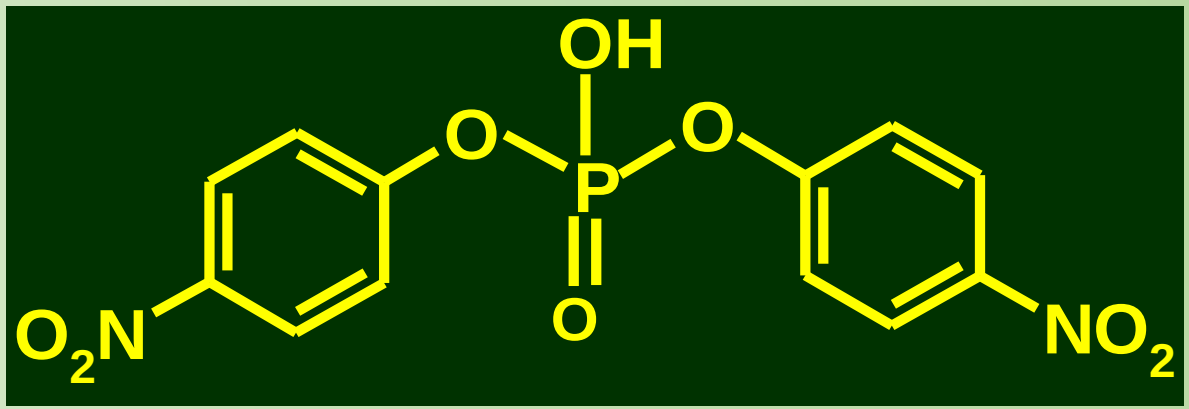
These are **Neurotoxic Compounds**

Phosphodiester bonds are extremely stable and are highly resistant toward hydrolytic processes

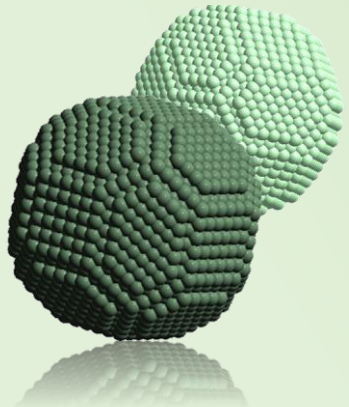




Bis-*p*-nitrophenyl Phosphate (BNPP) is a phophodiester compounds than can be used as a model molecule



The stability of this molecule is relatively high:



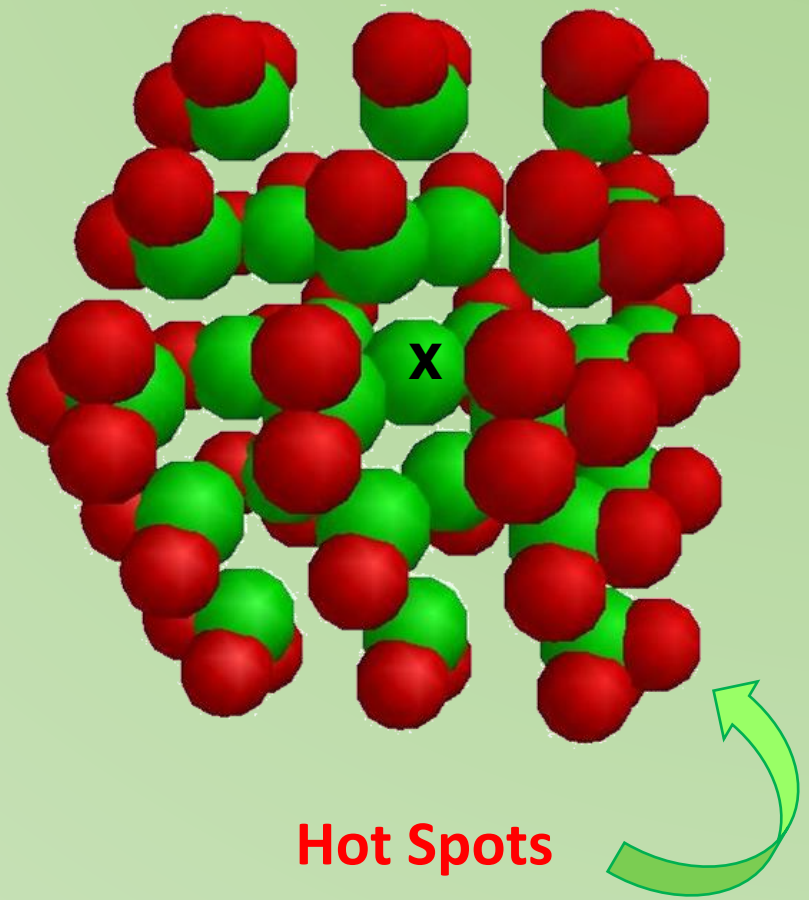
Its $t_{1/2}$ is 2000 years in water at 20 °C and 53 years in water at 50 °C.

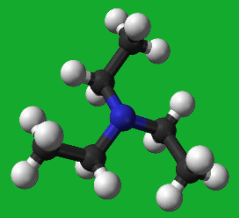
Chin, J.; Banaszczyk, M.; Jubian, V.; Zou, X. *J. Am. Chem. Soc.* 1989, *111*, 186

Zero-valent Iron Nanoparticles have a high potencial for hydrolyze phosphodiester bonds

This due to,

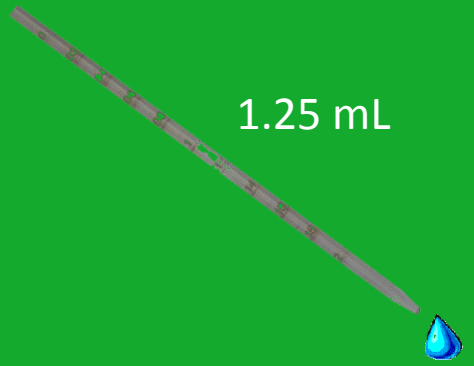
When is reducing the particle size, is increasing the surface area which has a direct influence on the number of active surface sites. These sites are called Hot Spots, where the electronic handness is very pronounced and are able to polarize bonds like P-O.





TEA

0.1 M en EG



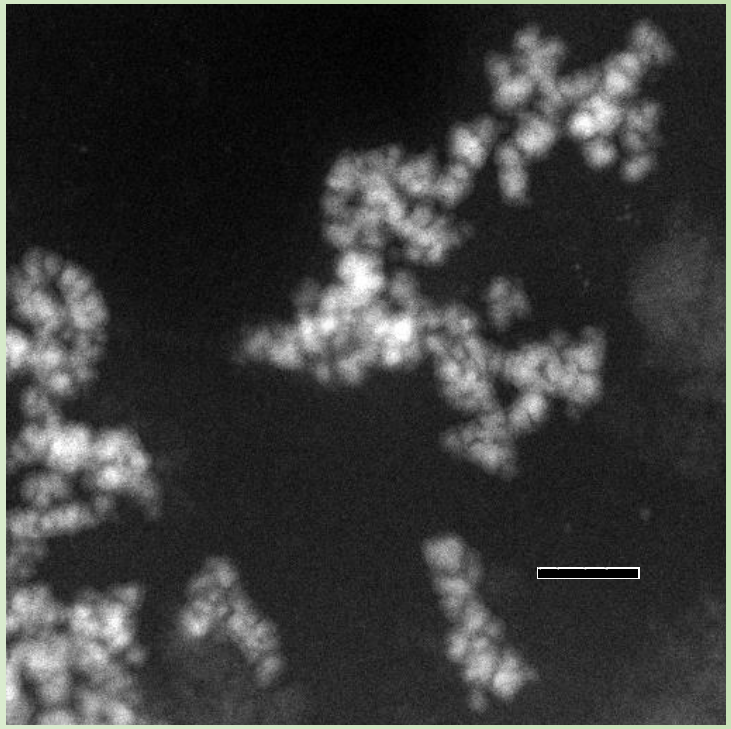
1.25 mL

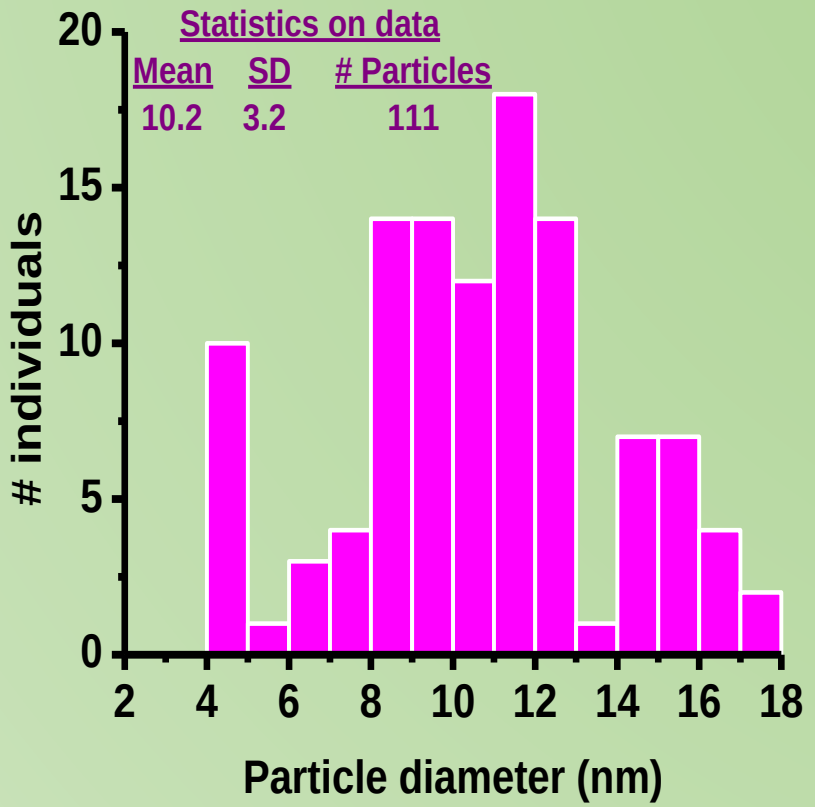
$NaBH_4$
Ethylene Glycol

Ethylene Glycol

$FeBr_2$
2.0×10^{-3} M

ZVI NPs Z-Contrast TEM micrographs

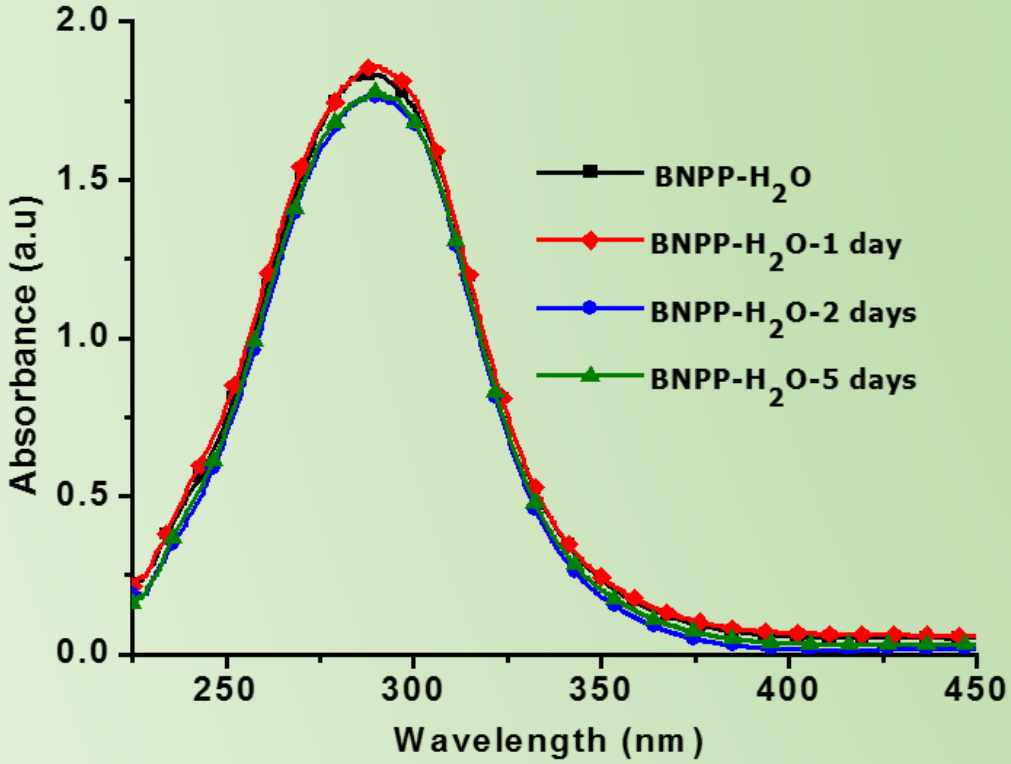




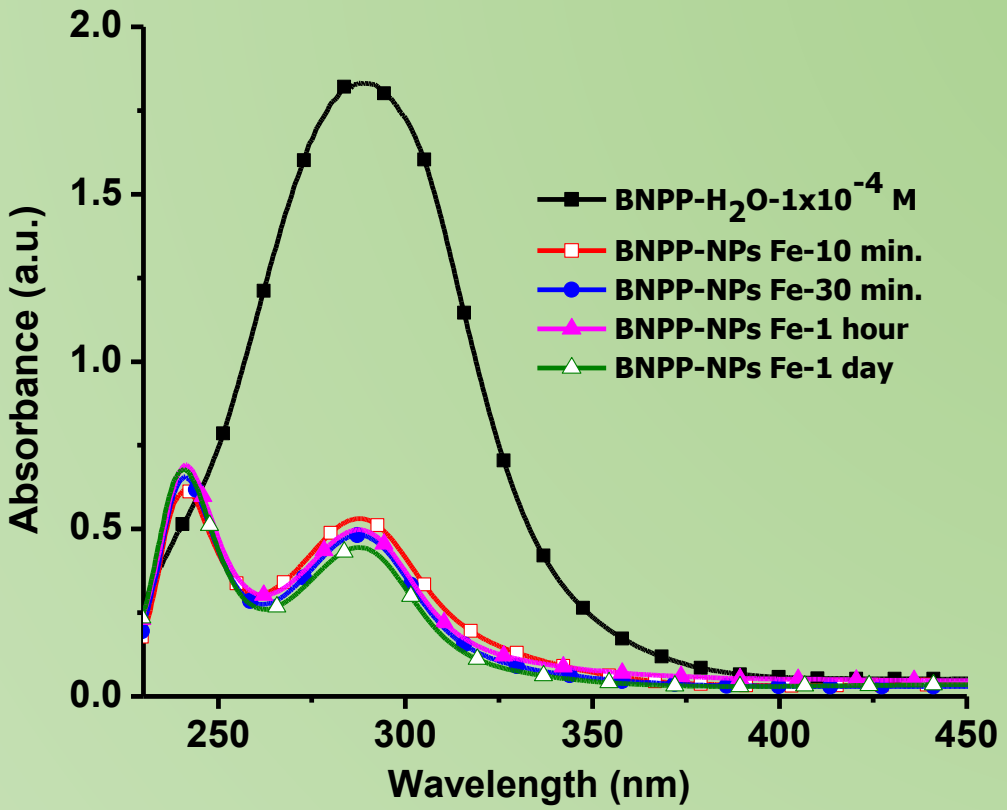
Z-Contrast of ZVI nanocrystallites prepared from $FeBr_2$ (2 x 10^{-3} M), $NaBH_4$ (2 x 10^{-2} M), and TEA (2 x 10^{-2} M) in EG and the corresponding particle size distribution histogram.

Parameters estimated of zero-valent Fe NPs dispersions from data of size distribution

Metal	Concentration of nanoparticles (particles/mL)	Total surface (m^2)	Relation Surface/volume (m^{-1})
iron	2.04×10^{13}	0.18	5.5×10^{8}

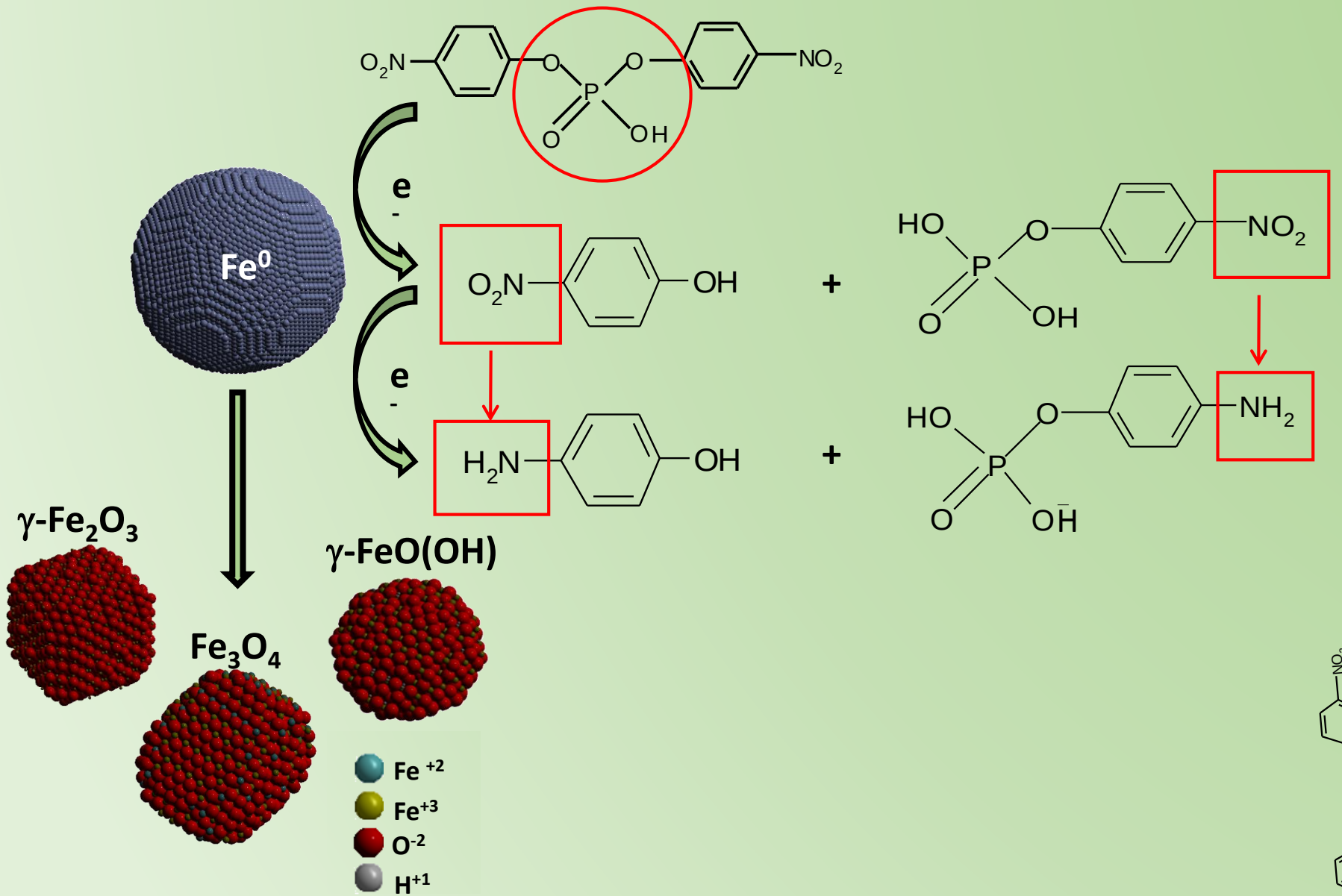


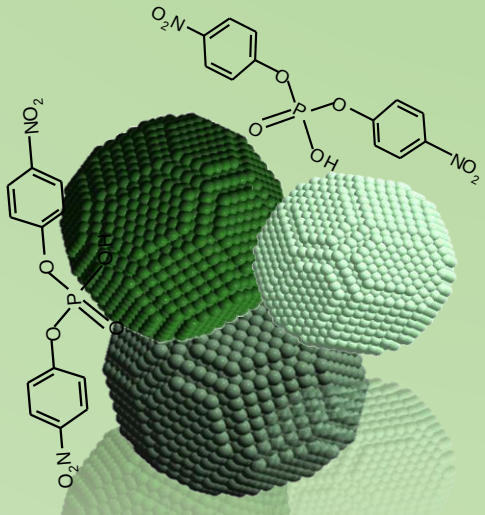
Electronic absorption spectra recorded at room temperature of a BNPP aqueous dissolution ($1x10^{-4}$ M).

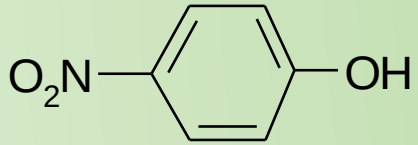


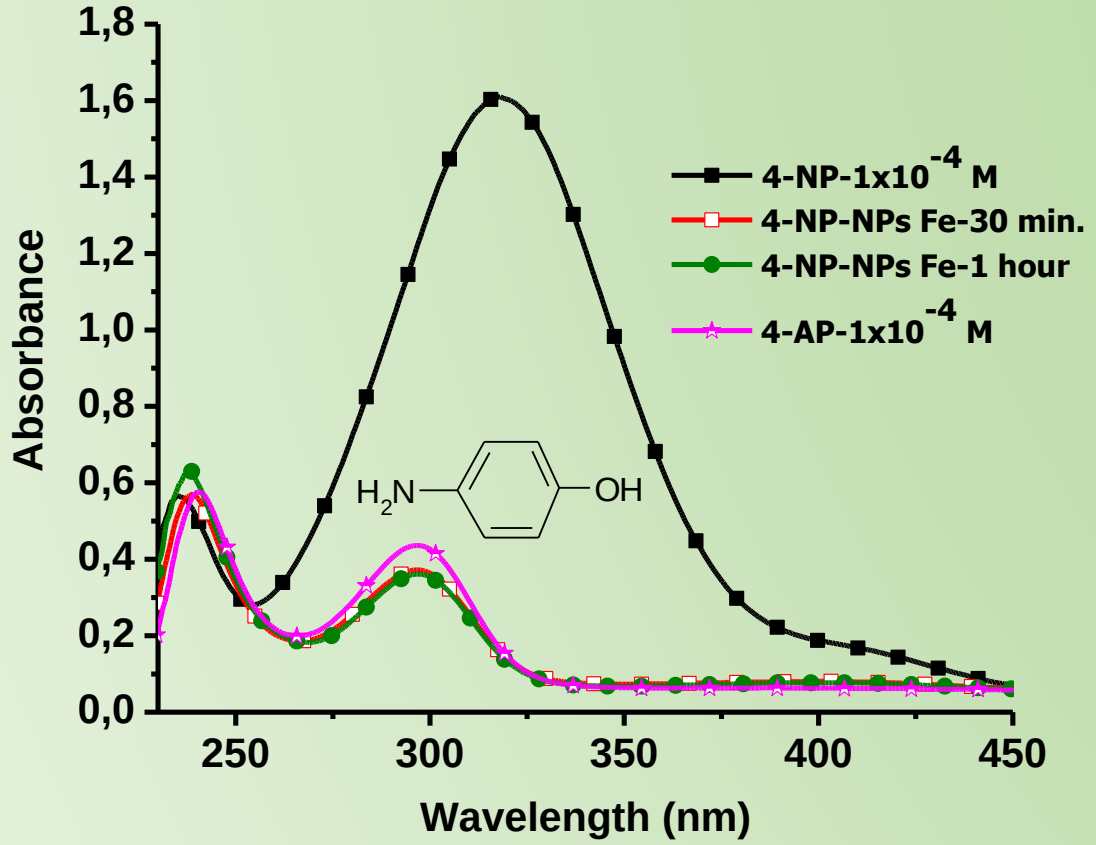
Time-dependent changes in the electronic absorption spectra of an aqueous reaction mixture, BNPP ($1x10^{-4}$ M) and ZVI NPs ($1x10^{-7}$ M).

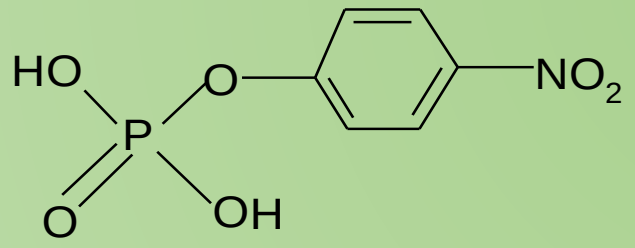
Proposed mechanism

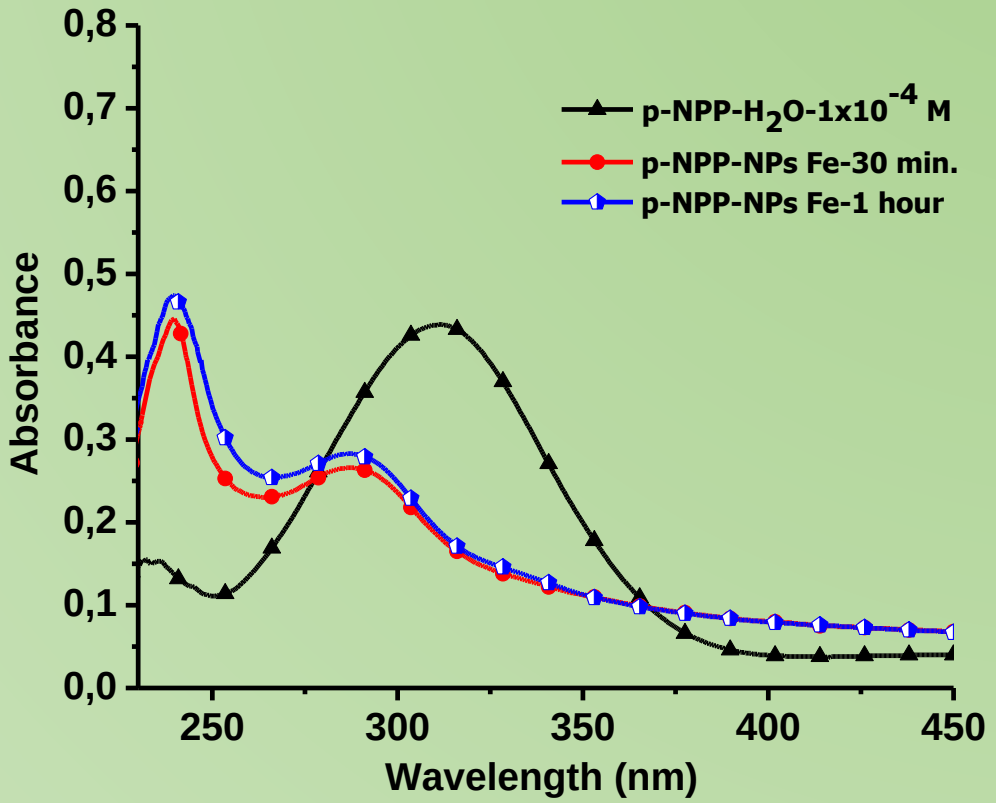


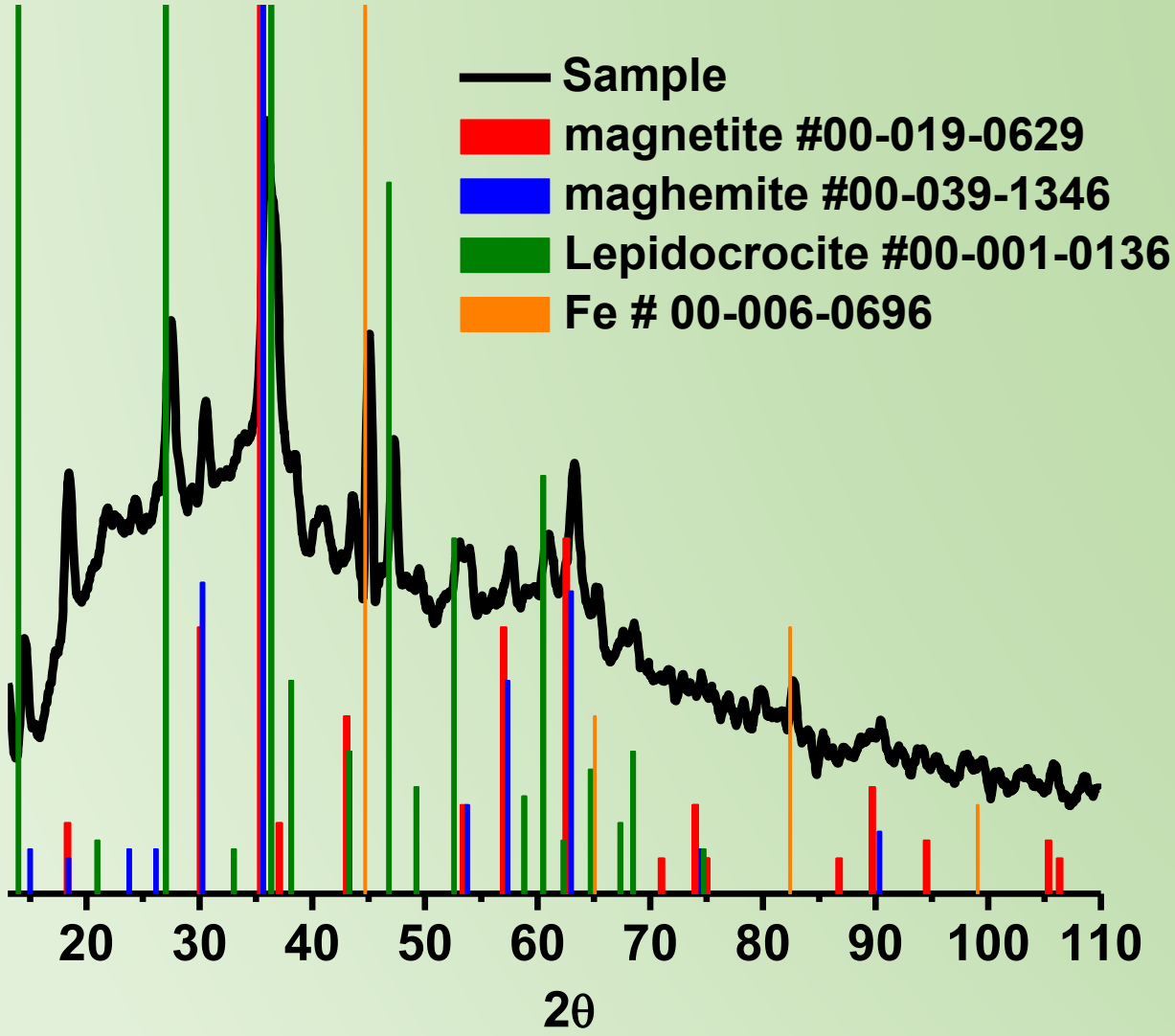



O_2N
OH

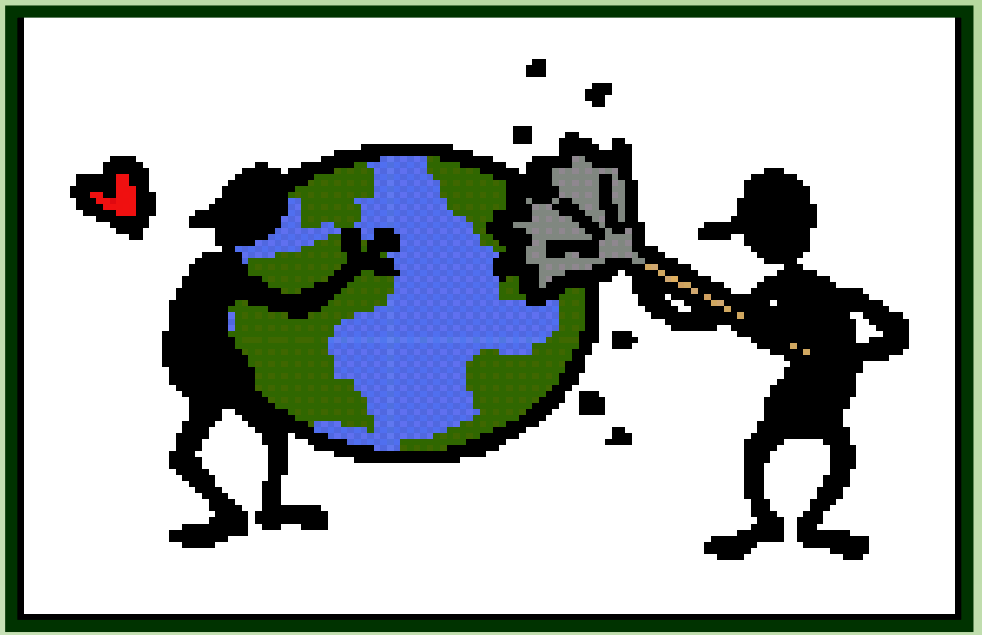

Absorbance
Wavelength (nm)
4-NP-1x10^{-4} M
4-NP-NPs Fe-30 min.
4-NP-NPs Fe-1 hour
4-AP-1x10^{-4} M
H_2N
OH


HO
O
NO_2
P
O
OH


Absorbance
Wavelength (nm)
p-NPP-H_2O-1x10^{-4} M
p-NPP-NPs Fe-30 min.
p-NPP-NPs Fe-1 hour



Iron by-products are environmentally friendly compounds since they are widely distributed in the Earth's crust.



Concluding remarks:

- **ZVI NPs with average diameter 10.2 nm (SD=3.3) were synthesized by a reliable method.**

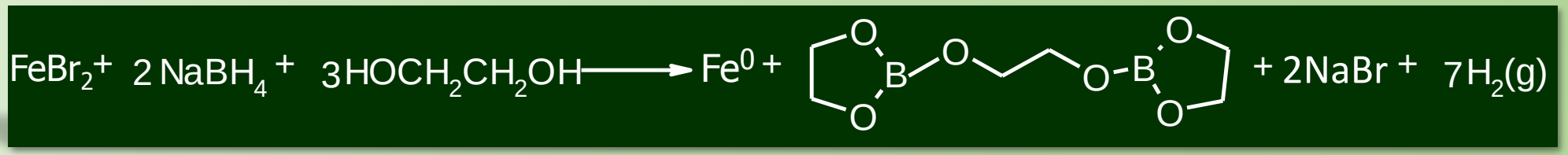
- **The ZVI nanocrystallines are able to degrade BNPP, under normal reaction conditions. The overall degradation process takes place in approximately 10 minutes.**

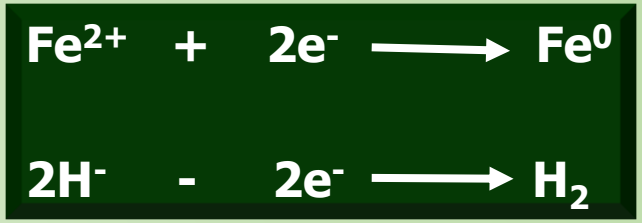
- **The by-products derivated from the ZVI nanoclusters are environmental friendly.**

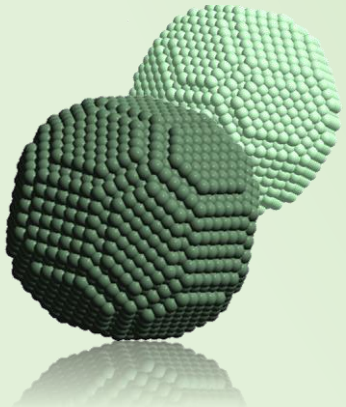
- **The by-products of BNPP are aromatic amines, which are more susceptible to biodegradation than the original nitro compounds.**

Thank you for your attention!!!

General Reaction Scheme of Synthesis of ZVI NPs







Conditions:

Room Temperature

Argon bubbling