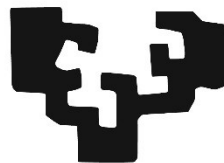


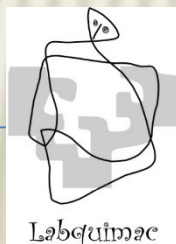
eman ta zabal zazu



Universidad
del País Vasco

Euskal Herriko
Unibertsitatea

NANOTECHNOLOGY AS TOOL FOR SOIL RECOVERY



Labquimac

José Luis Vilas Vilela

Departamento de Química Física

Laboratorio de Química

Macromolecular

UPV/EHU

“NANO”:

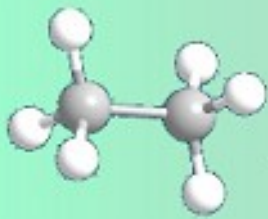


Prefijo de etimología griega que indica una medida (significa diminuto, enano, pequeño)

$$\mathbf{1\ nm = 10^{-9}\ m = 0'001\ \mu m}$$

Escala nanométrica

(0.2 – 100 nm)



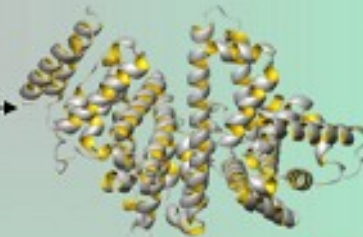
Enlace C-C
0.15 nm



Hélice α
0.50 nm



Nanotubo
de
carbono
1 nm



Albúmina
8 nm



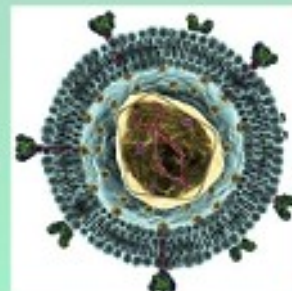
Membrana
celular
10 nm



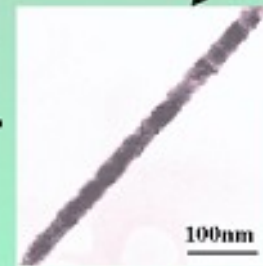
Cabello
humano
80 μm



Eritrocito
8 μm



Virus VIH
90 nm



Nanocable
típico
10 nm

NANOSCALE ADVANTAGES

Relative Surface Increase



Increase in

CHEMICAL REACTIVITY

Quantic Effects

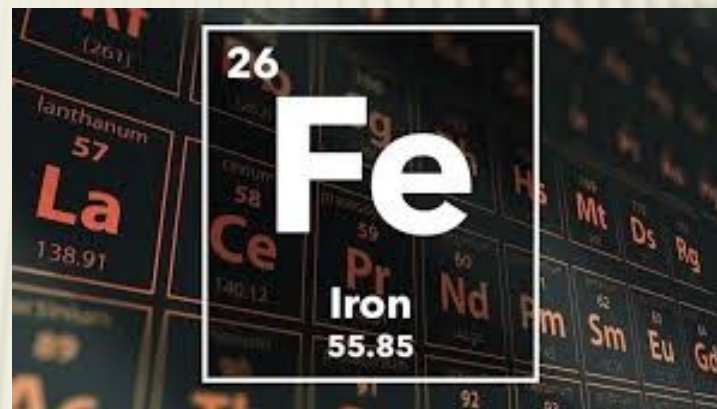


Change in properties

**Optical
Magnetic
Electrical**

.....

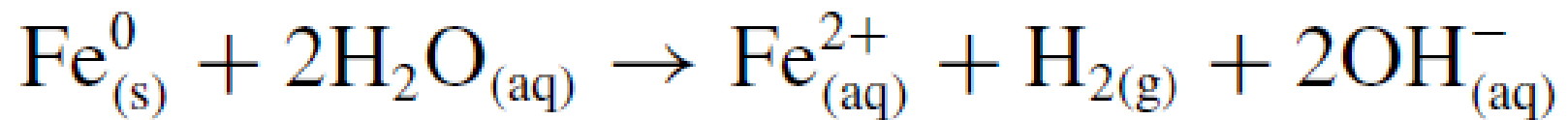
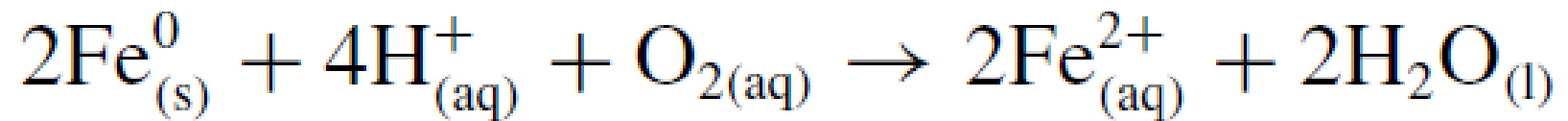
ZERO-VALENT IRON



Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron

Vol. 32, No. 6—GROUND WATER—November-December 1994

by Robert W. Gillham and Stephanie F. O'Hannesin^a



ZERO VALENT IRON

- **Las técnicas actuales de tratamiento de suelos contaminados y de aguas subterráneas no son eficaces en muchas situaciones, lo que ha conducido a un aumento de la investigación para el desarrollo de una alternativa, tanto para remediación in situ como para el desarrollo de tecnologías de tratamiento ex-situ para la recuperación de suelos y aguas contaminadas.**
- **Las técnicas de remediación alternativas utilizan las propiedades reductoras del hierro para eliminar o estabilizar contaminantes inorgánicos, orgánicos y radiactivos.**
- **La capacidad reductora del hierro cero-valente (ZVI) comenzó a ser evaluada por su capacidad de tratar una amplia gama de contaminantes peligrosos a principios de los años 90.**
- **El empleo más común de ZVI ha sido en barreras permeables reactivas (PRBs) diseñadas para interceptar plumas de contaminación en la subsuperficie y así remediirla. Este sistema de tratamiento pasivo ha sido usado para tratar agentes contaminantes, como hidrocarburos tratados con cloro, nitroaromaticos, policlorobifenilos(PCBS), pesticidas e incluso cromatos.**

PERMEABLE REACTIVE BARRIER



a)



b)



c)



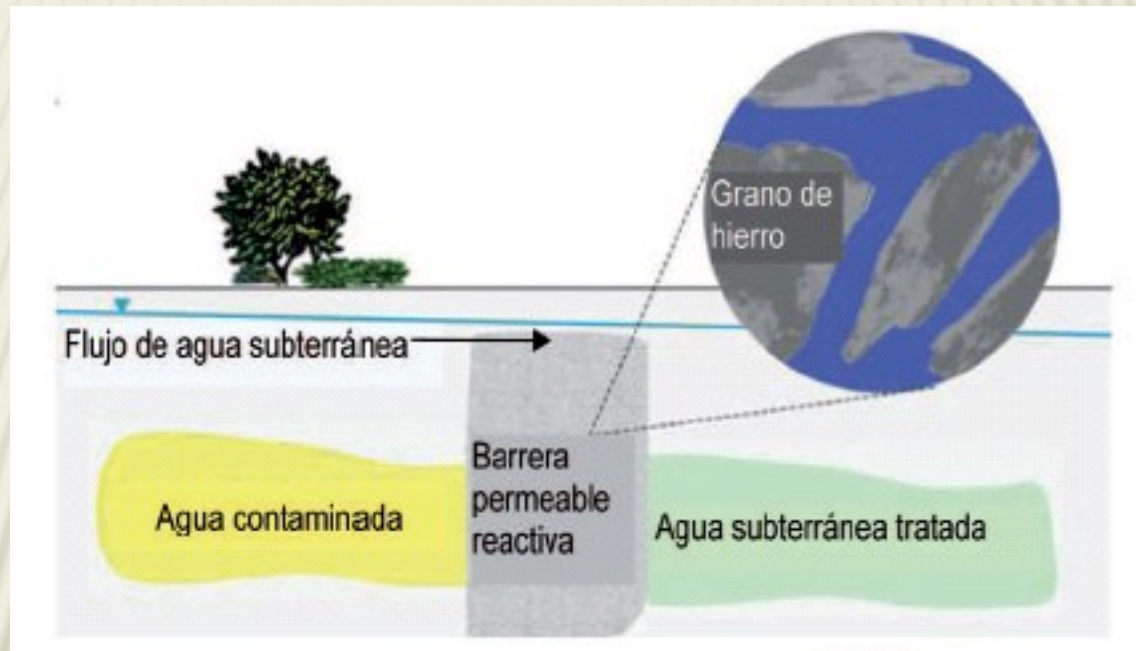
d)

Figure 4-1. Examples of ZVI and ZVI emplacement: (a) fine-grained ZVI, (b) coarse-grained ZVI being placed in a trenched PRB, (c) microscale ZVI in an injectable EHC[®] slurry, and (d) installation of ZVI PRB at a U.S. Coast Guard facility using a one-pass trencher.

*ITRC –
Permeable
Reactive
Barrier:
Technology
Update June
2011*

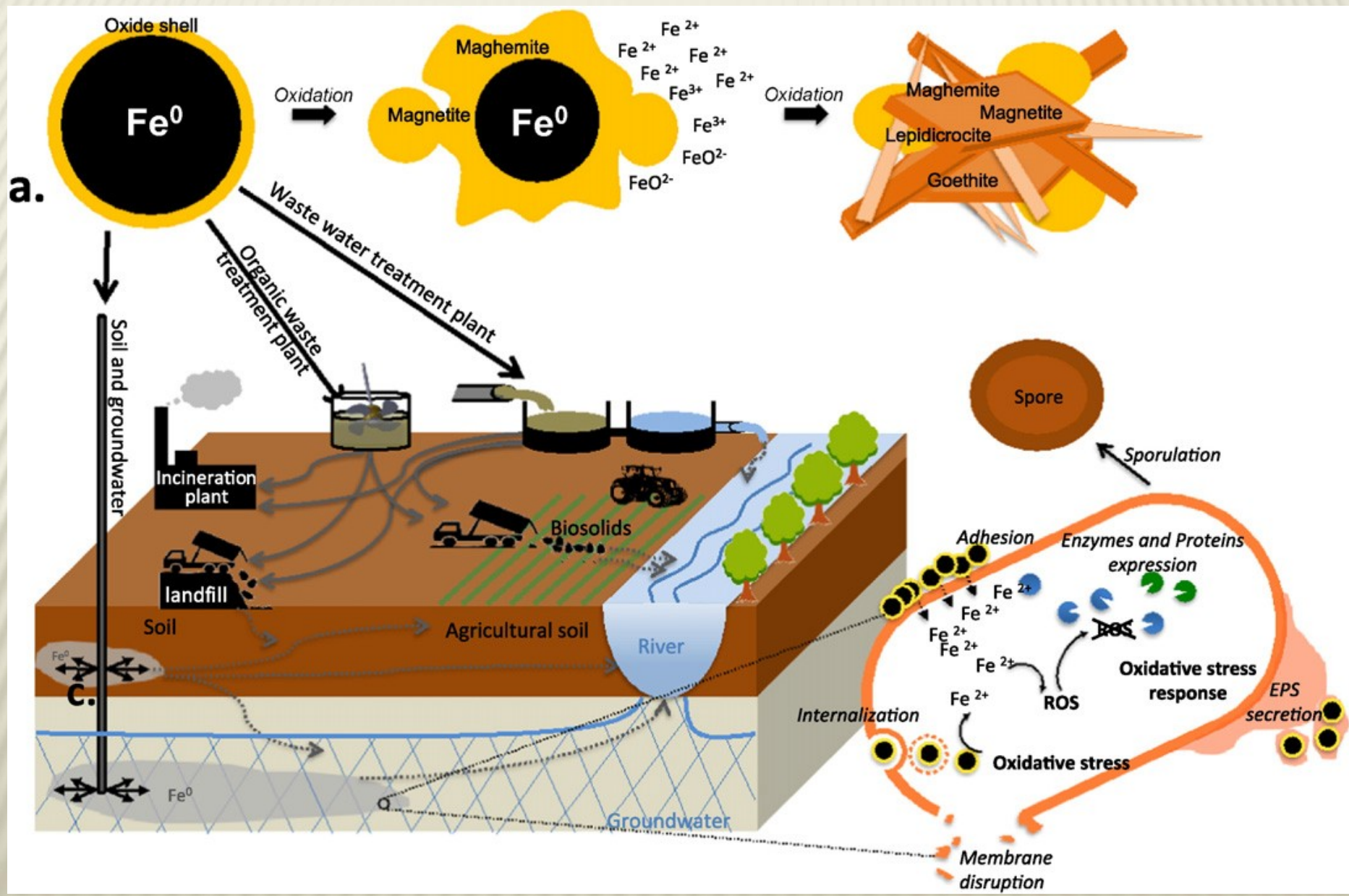
PERMEABLE REACTIVE BARRIER (PRBS)

Fe (10-100 μm)



desadvantages:

- Its installation require intrusive methods.
- It requires flow paths that can only direct the contaminants that flow through the barrier.
- Loss of reativity and increasement in the precipitacion.



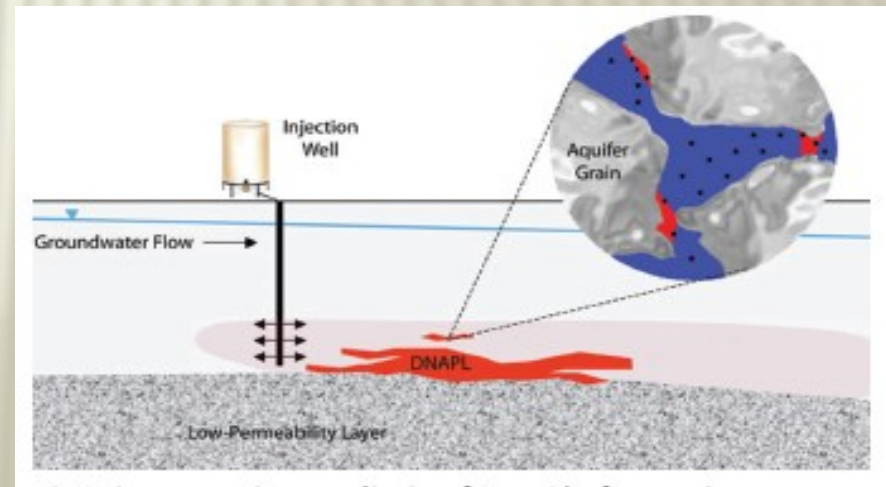
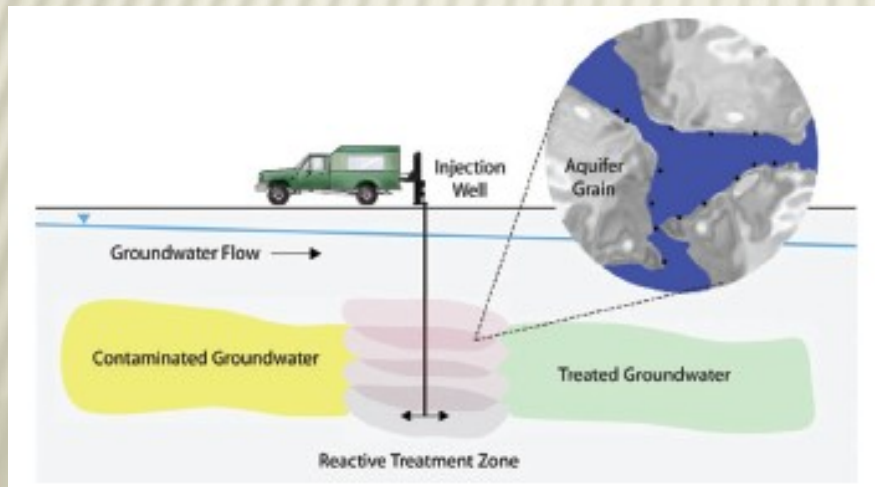
➤ Why go nano?

	Micro ZVI	Nano ZVI
Particle size	10 – 100 μm	50 – 75 nm
Surface area	10 m^2/Kg	30,000 m^2/Kg
Cost	~ 1 €/Kg	~ 50 €/Kg
Actual cost	10 $\text{m}^2/\text{€}$	600 $\text{m}^2/\text{€}$

ZERO-VALENT IRON

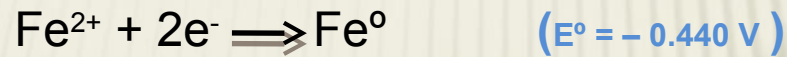
NANOIRON TECHNOLOGY (nZVI):

- Fast (and furious) reaction:
 - + Reduction in the treatment time
 - + Low cost
 - + Decreases the exposure time of workers, and of flora and fauna
- It reduces itself totally without toxic products
- in situ treatment
 - + Less devices and equipments

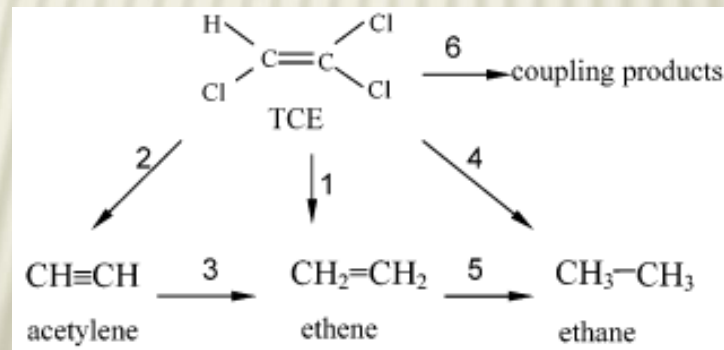
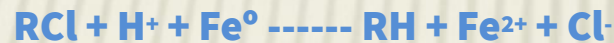


NANOHIERRO (NZVI) REACTIVIDAD:

- Fe⁰ posee una fuerte tendencia a donar electrones a un electron-aceptor.



- La reacción del ZVI con los hidrocarburos clorados (RCl) es termodinámicamente favorable:



**Applications of stabilized nZVI for
transformation of organic contaminants**

**Applications of stabilized nZVI for
removal/immobilization of inorganic contaminants**

NANOIRON

nZVI have demonstrated a broader range of treatment capability for contaminants :

Trihalometanos:

Bromoformo,
dibromoclorometano,..

Pesticidas organoclorados
(DDT, Lindano)

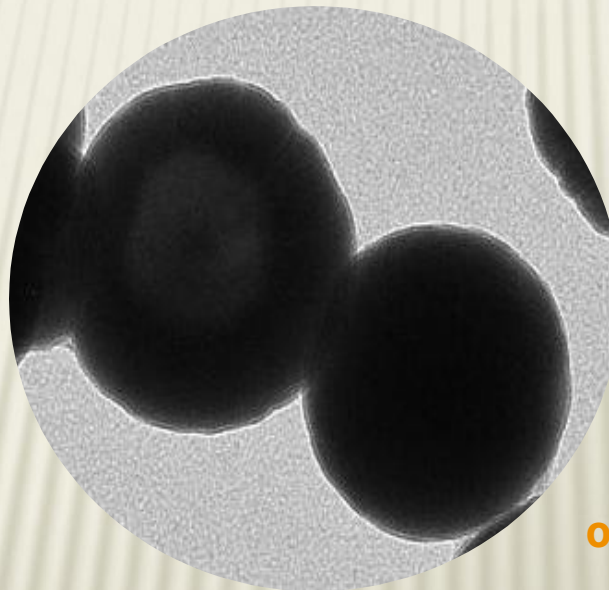
Clorobencenos
(hexaclorobenceno,
pentaclorobenceno
...)

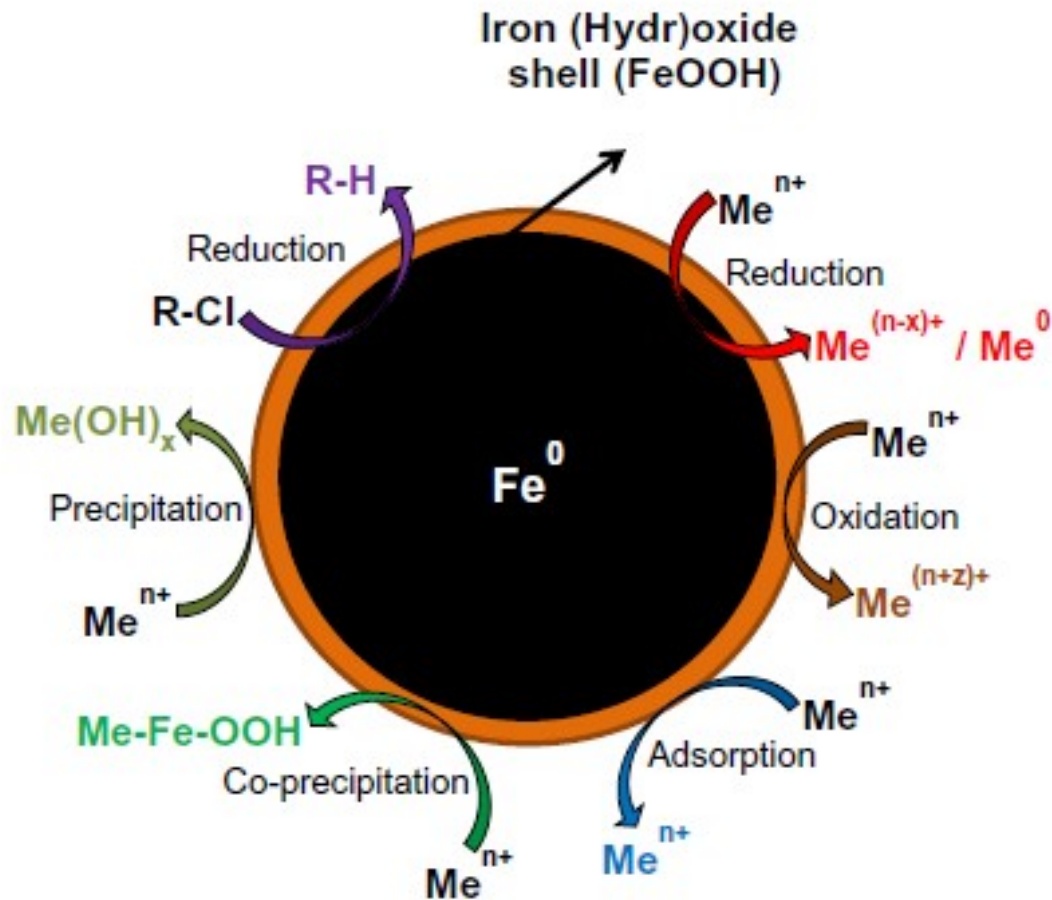
Metales pesados
(Cr VI, Hg²⁺, Cd²⁺, Pb²⁺, Ni²⁺)

PCBs, aniones inorgánicos
(perclorato, nitrato)

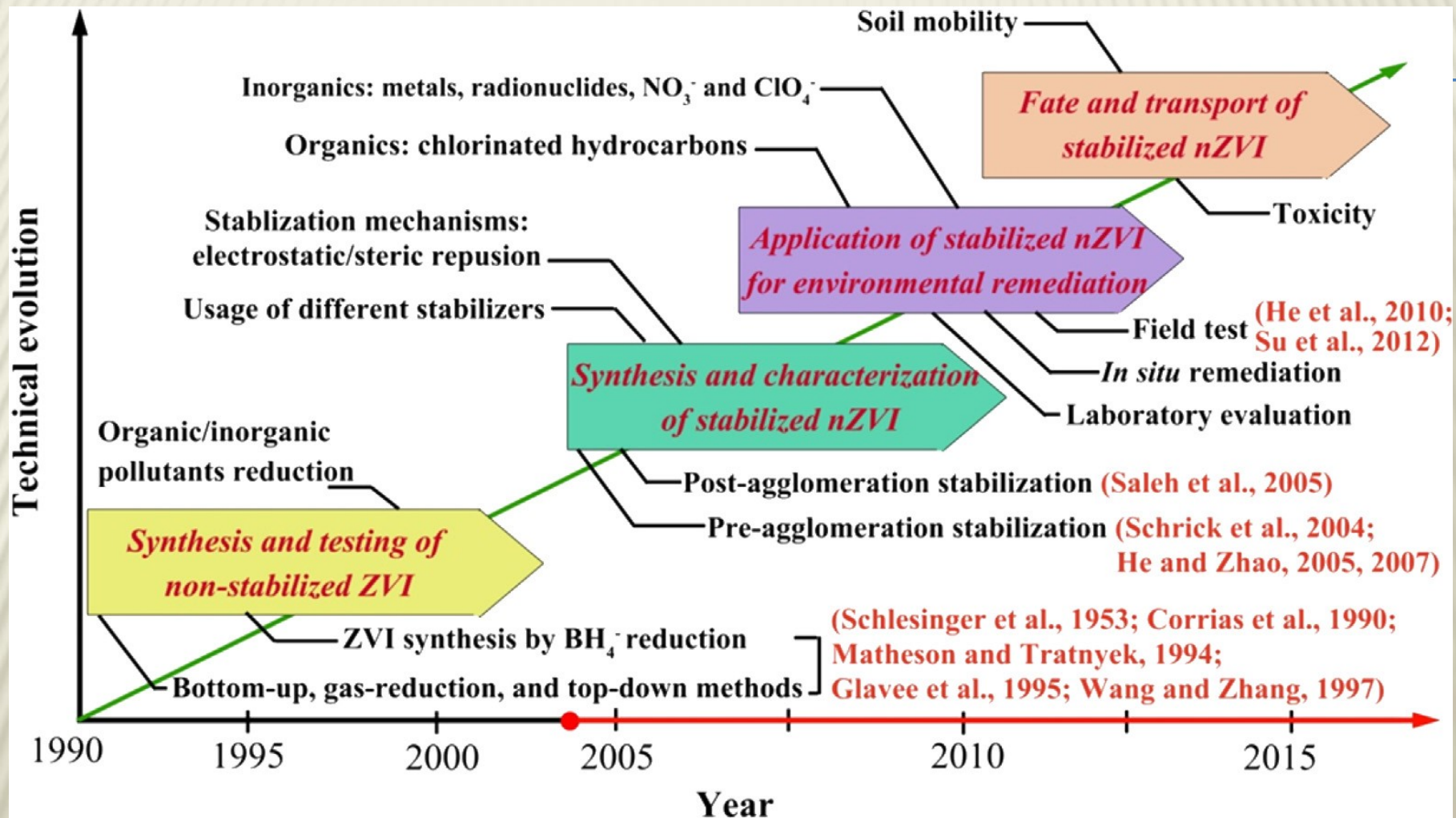
Otros disolventes clorados

(Cloroformo, PCE,
Diclorometano,
Tetracloruro de carbono...)





Core-shell structure of nZVI depicting various mechanisms for the removal of metals and chlorinated compounds (O'Carroll et al. 2013, adapted from Li et al. 2006).

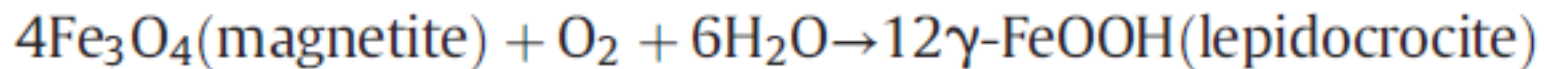
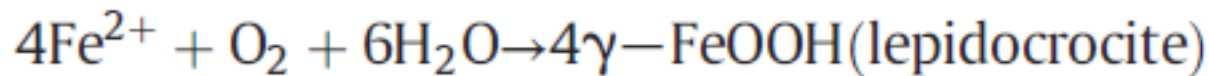
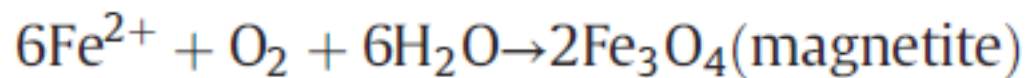
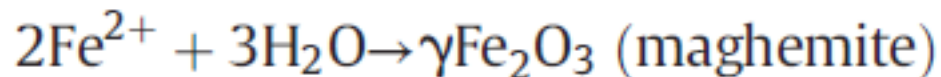


Development and technical evolution of stabilized nZVI technologies
 Water Research 100 (2016) 245-266

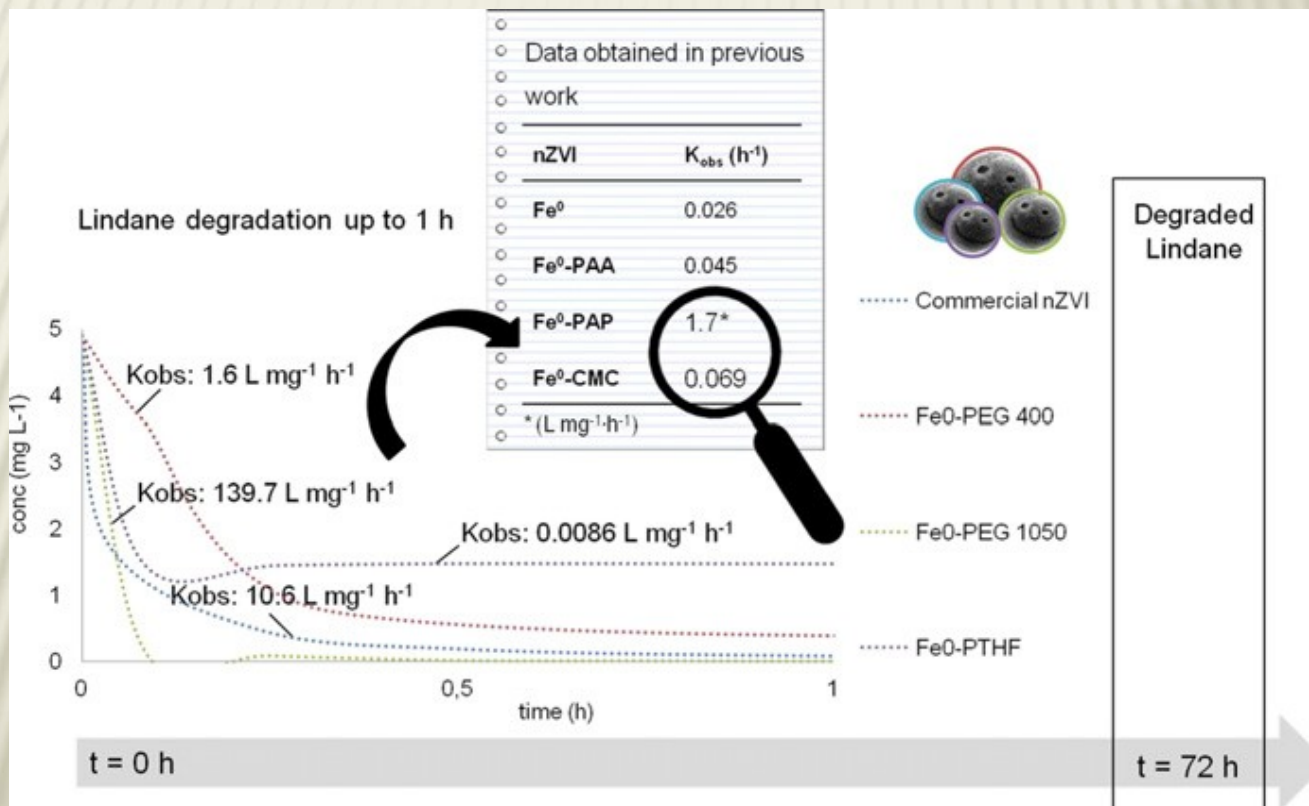
ESTIMATED COSTS*

❖ Remedial Approach	❖ Estimated Cost
1. Pump and Treat	➤ \$4,160,000
2. Reactive Barrier	➤ \$2,200,000
3. NanoFe TM	➤ \$ 450,000

*H.S. Gill, PARS Environmental Inc. (USA)



ENVIRONMENTAL APPLICATIONS OF ZERO VALENT IRON NANOPARTICLES: THE LINDANE CASE



Objective:

Development of a new technology that provides greater efficiency for its application both in-situ and ex-situ in the remediation of contaminated soils and effluents.

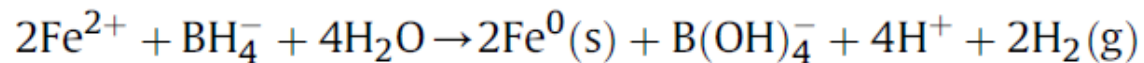
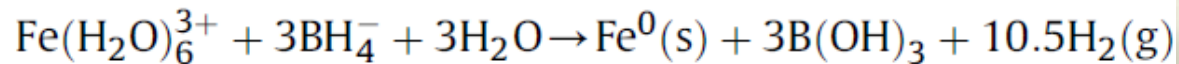
Optimize the synthesis by getting an active material against the greatest amount of pollutants

Ensure that the material is stable for the necessary time, in order to use it for in-situ treatments

Synthesize a material with a high dispersion capacity through the soil in order to increase the effectiveness of the treatment

SYNTHESIS OF IRON DE NANOPARTICULES (nZVI)

Synthesis of nZVI by reduction of iron ions in aqueous solutions using sodium borohydride :



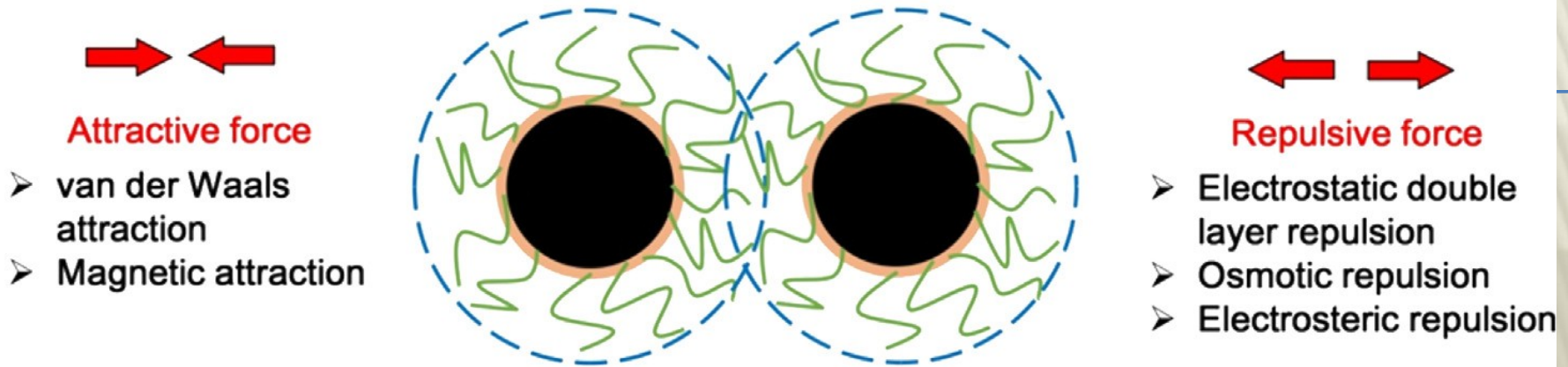
He, F., Zhao, D., 2005. Environ. Sci. Technol. 39 (9), 3314-3320.

He, F., Zhao, D., 2007. Environ. Sci. Technol. 41 (17), 6216-6221.

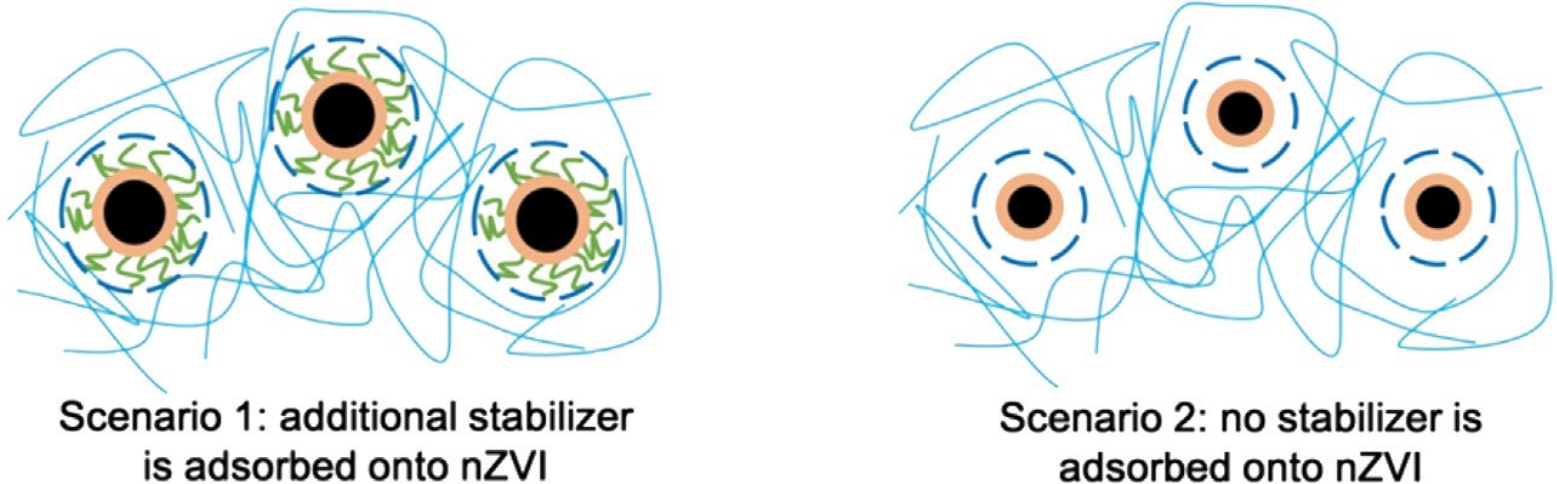
General procedure:

- * Inert atmosphere
- * constant agitation 400 rpm
- * Reaction time= 30min

(a) Surface modification stabilization



(b) Network stabilization



Schematic representation of (a) surface modification stabilization (where surface coating facilitates particle repulsion), and (b) network stabilization (where a medium network is formed due to hydrogen bonding and polymer entanglements).

SYNTHESIS OF nZVI

REACTANTS

Nombre	Fórmula molecular	Peso molecular (g/mol)	Pureza %	Casa comercial
Cloruro de hierro (II) tetrahidratado	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	198,81	99	Sigma Aldrich
Borohidruro sódico	NaBH_4	37,83	98	Sigma Aldrich

SYNTHESIS OF nZVI

❖ Evaluated parameters:

- ① Reaction time and stirring
- ② Order of addition and stoichiometry of reagents
- ③ Atmosphere: N_2 or Air
- ④ Number of washes
- ⑤ Handling nZVI: drying in the oven, vacuum drying, ultrasonic

SYNTHESIS OF nZVI

Techniques of characterization

- ❖ X Ray Diffraction
- ❖ SEM
- ❖ Magnetometry
- ❖ TEM

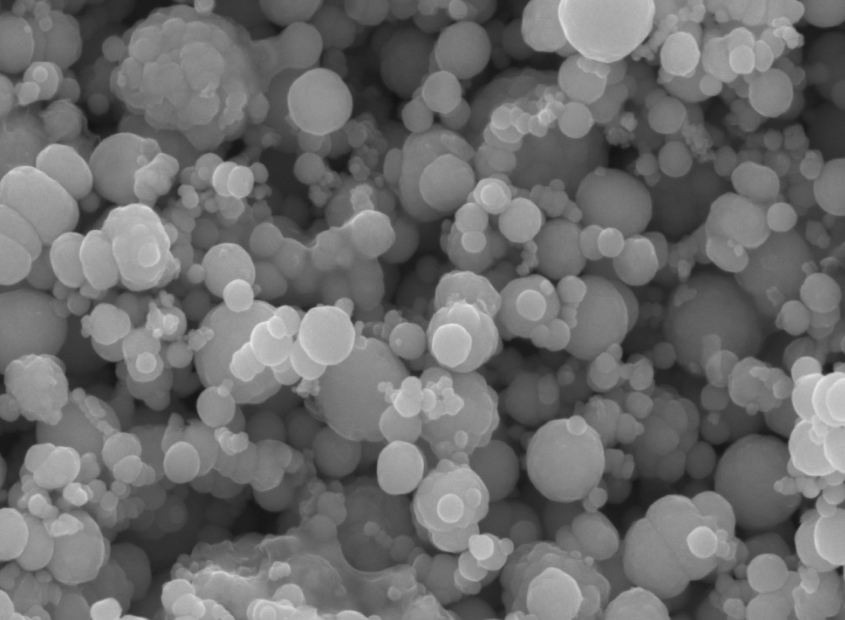
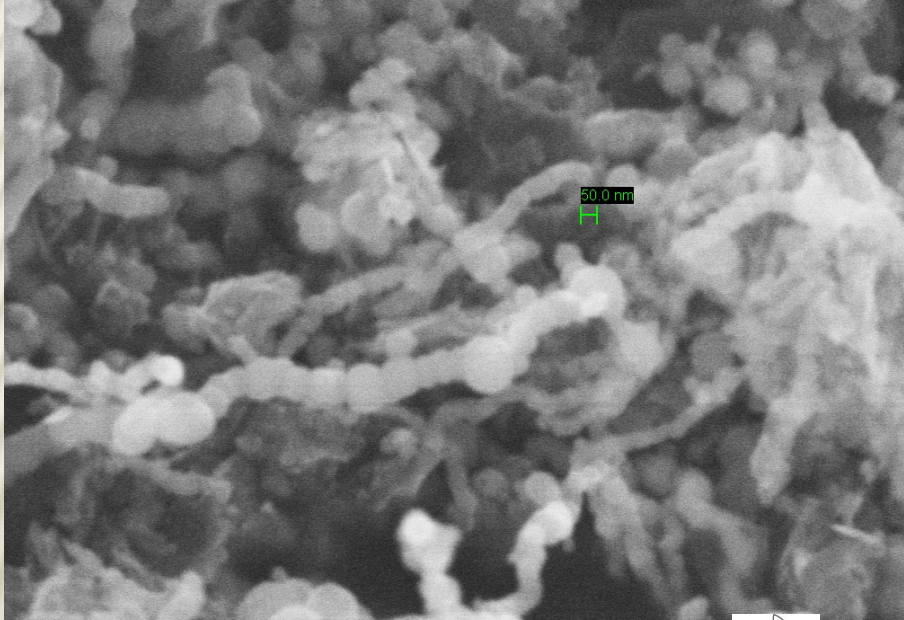
SYNTHESIS OF nZVI

Muestra	Tamaño medio (nm)	Agitación (rpm)	Tpo inyecc. (min)	[FeCl ₂] (M)	[NaBH ₄] (M)	Ms (emu/g)
A12	81,3	500	5	0,060	0,543	162,73
A13	115,9	500	5	0,060	0,528	146,82
A14	88,8	400	5	0,062	0,592	110,39
A19	70,4	500	5	0,060	0,538	96,85
A21	70,5	500	4	0,030	0,611	53,33
A22	85,4	100	4	0,030	0,538	62,97
A29	59,4	500	2	0,060	0,549	130,29
A30	74,8	500	19	0,030	0,539	69,86
A31	83,1	100	43	0,030	0,560	99,67

SYNTHESIS OF nZVI

360 rpm

500 rpm

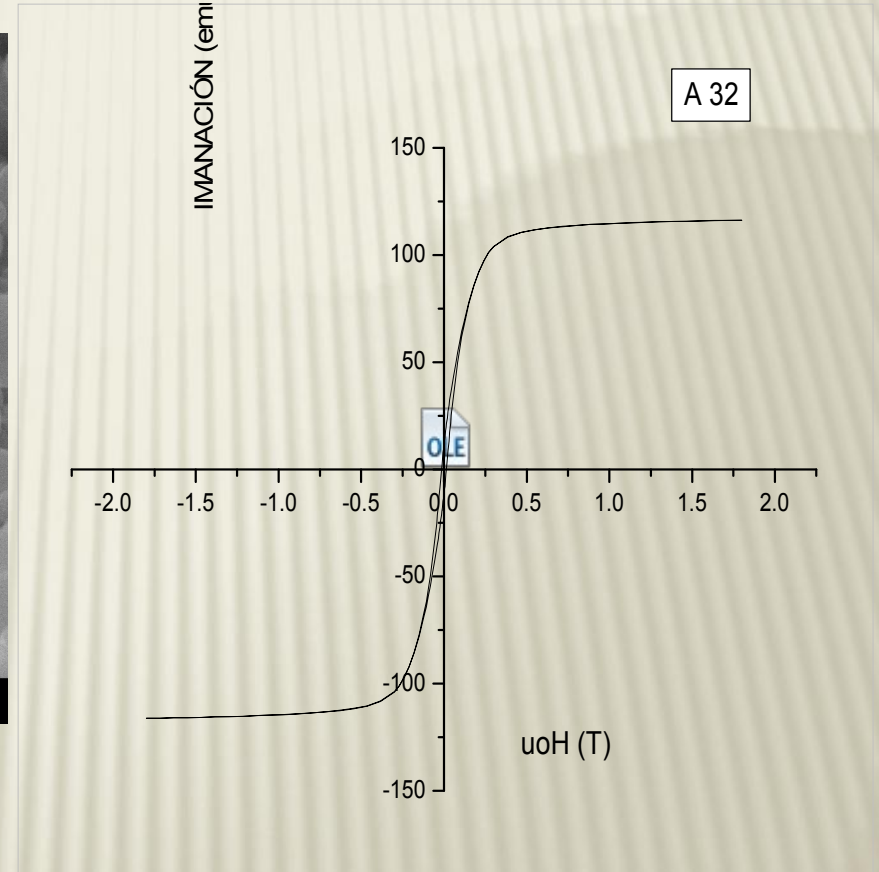
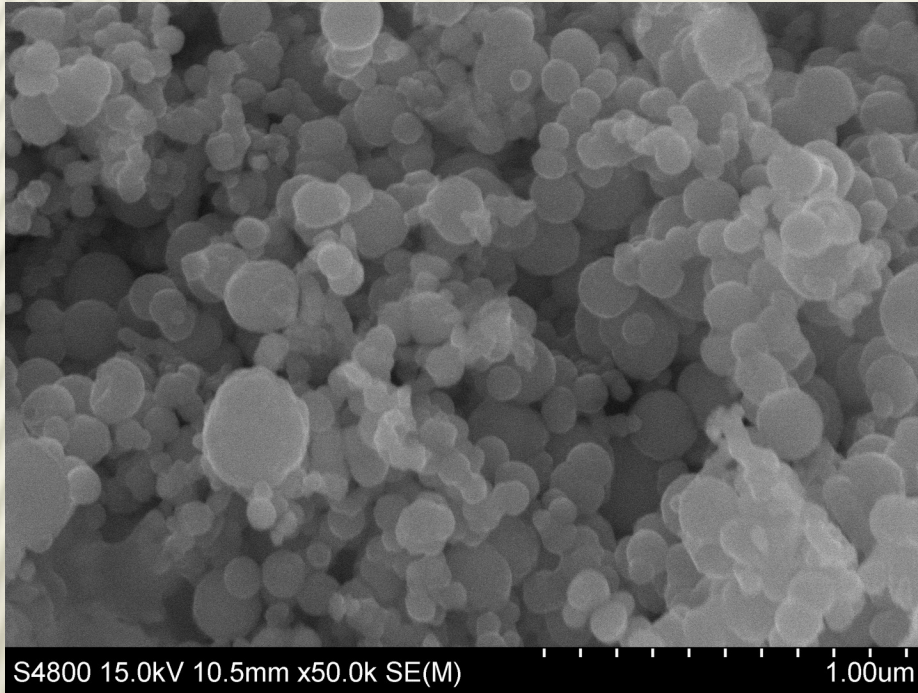


200 nm 20.00 kV SE1 File Name = Fe NP A_03.tif 1 A
WD = 4.5 mm Mag = 97.27 K X



UPV/EHU SEI 10.0kV X50,000 100nm WD 6.0mm

A-32



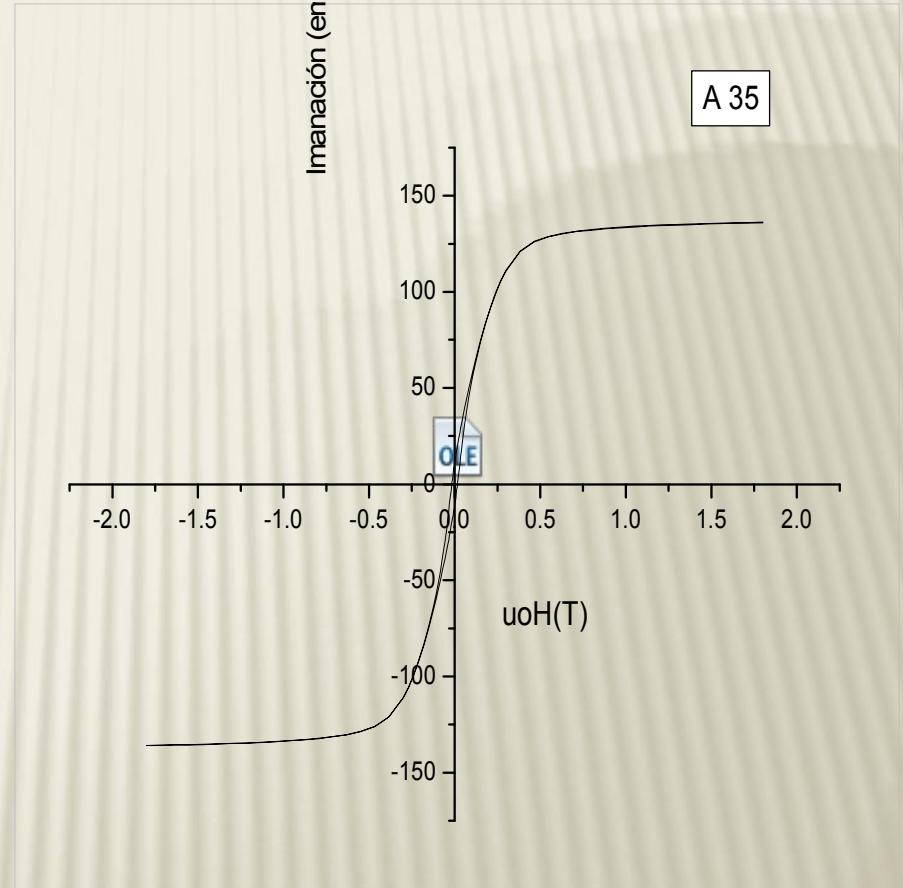
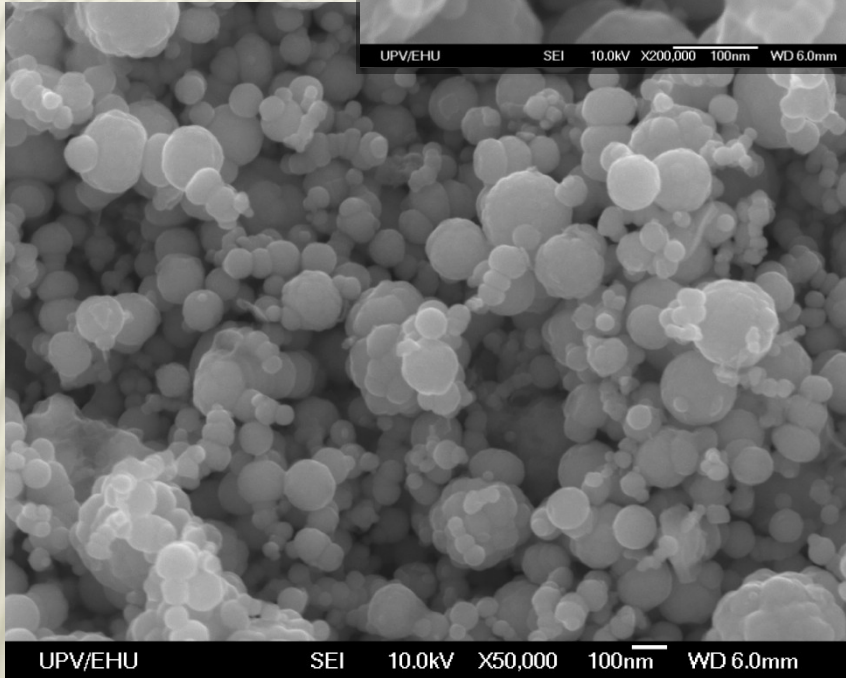
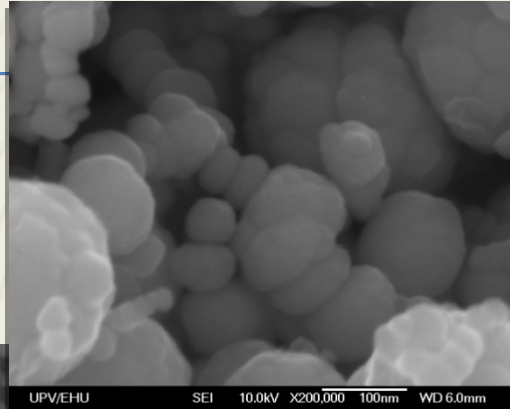
MS=116,23 emu*g⁻¹

ATMÓSFERA DE AIRE

SYNTHESIS OF nZVI

M	[FeCl₂] (mol*l⁻¹) (1)	[NaBH₄] (mol*l⁻¹) (2)	Relación 1:2
A 35	0,06	0,20	1:3
A 36	0,06	0,37	1:6
A 37	0,06	0,24	1:4
A 38	0,06	0,30	1:5
A 39	0,06	0,42	1:7

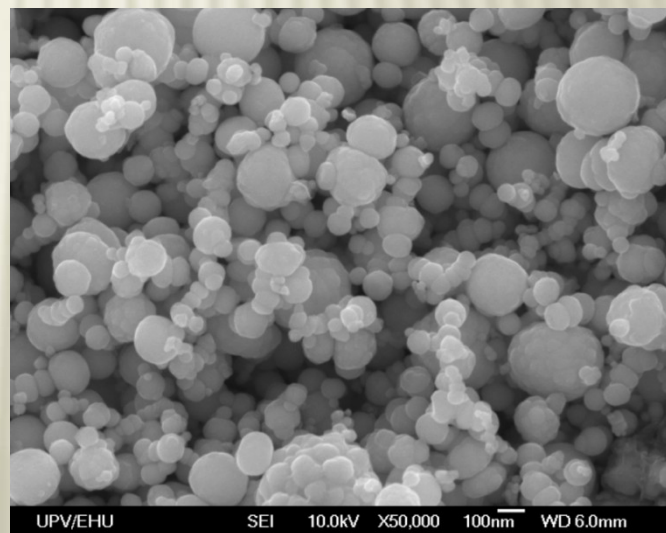
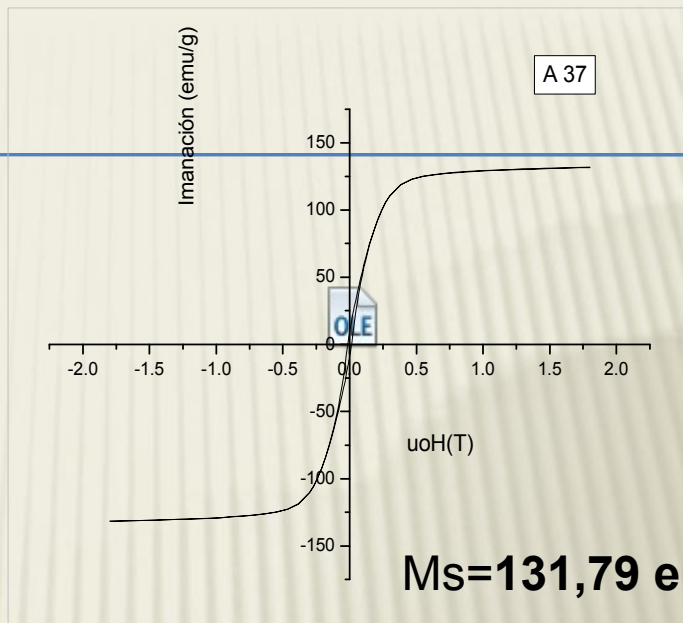
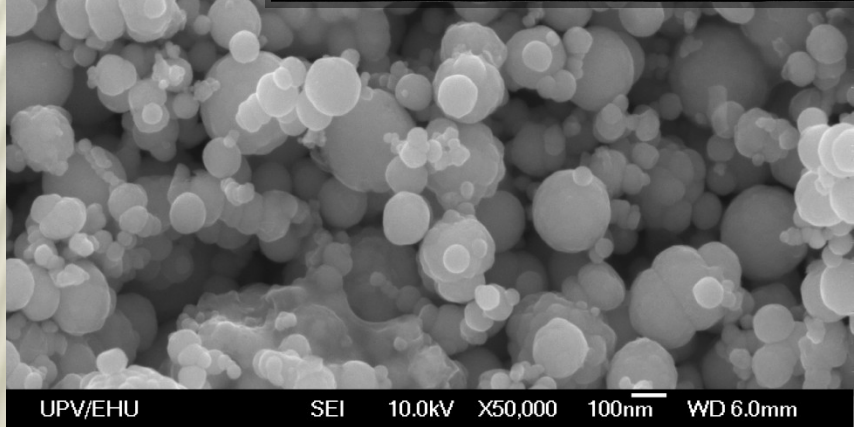
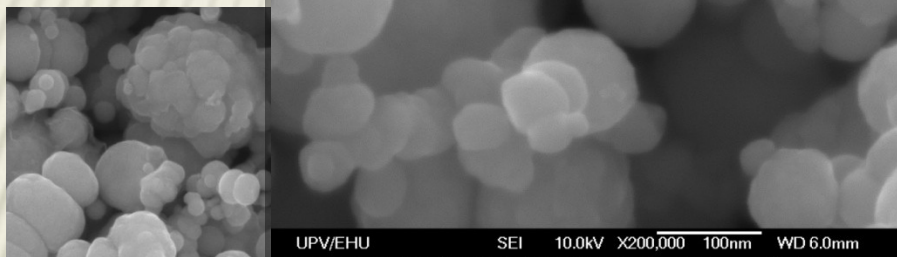
A-35



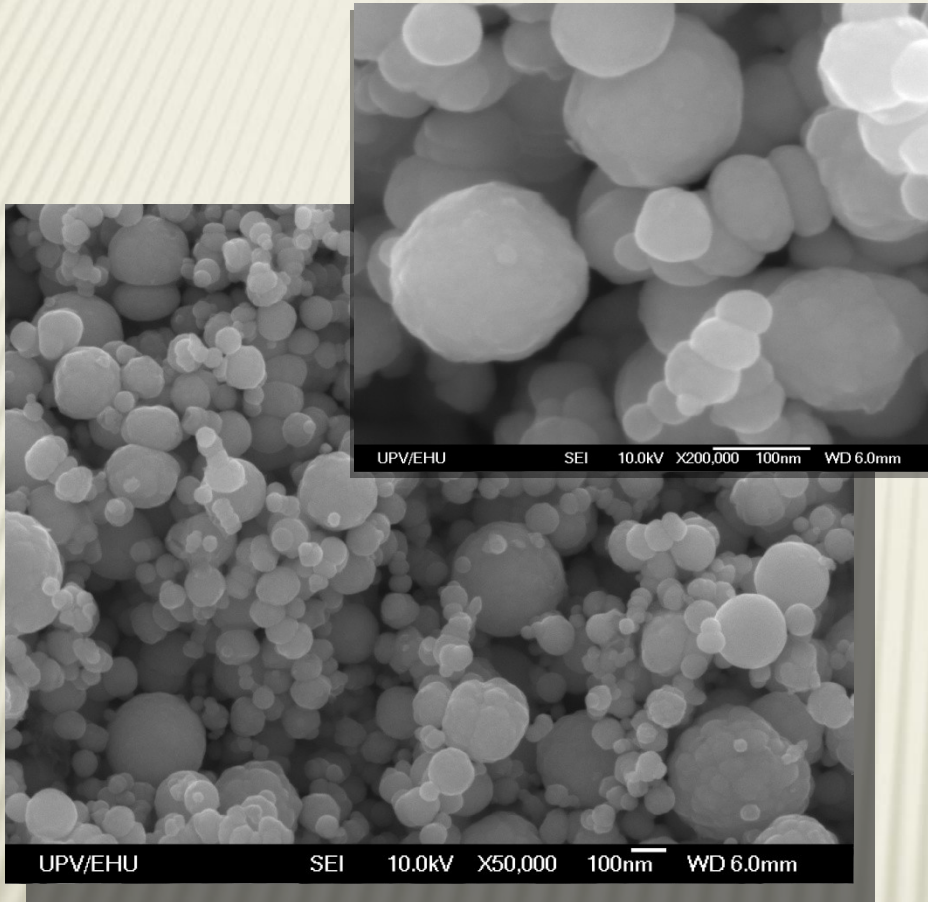
$M_s = 136,24 \text{ emu} \cdot \text{g}^{-1}$

Relación $\text{FeCl}_2 : \text{NaBH}_4 = 1:3$

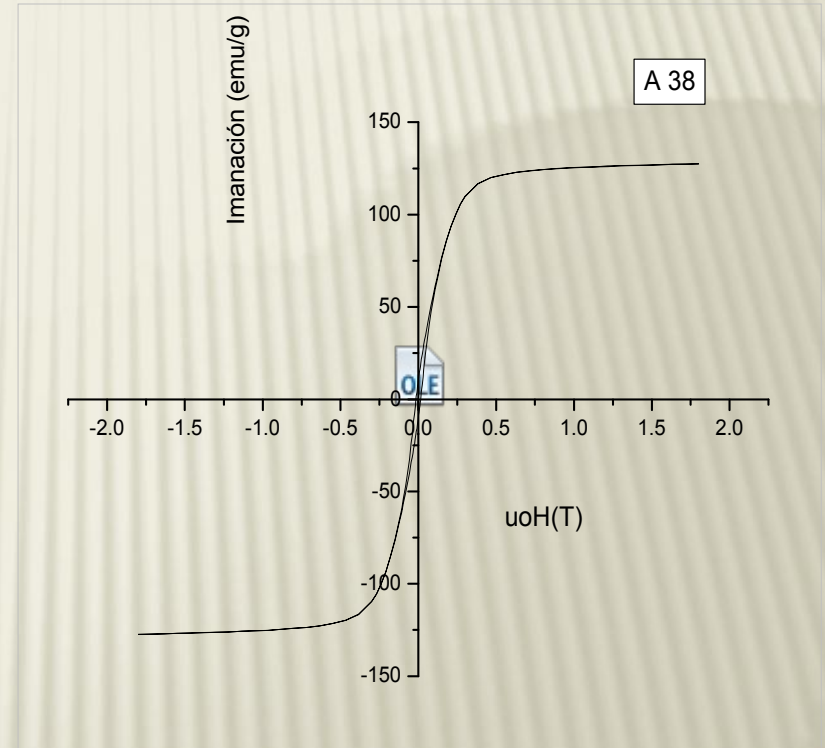
A-37



Relación FeCl_2 : $\text{NaBH}_4 = 1:4$



Relación FeCl_2 : NaBH_4 = 1:5

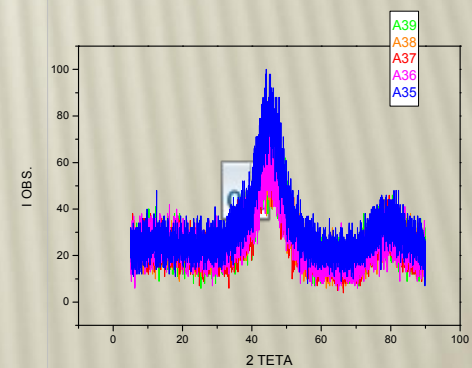
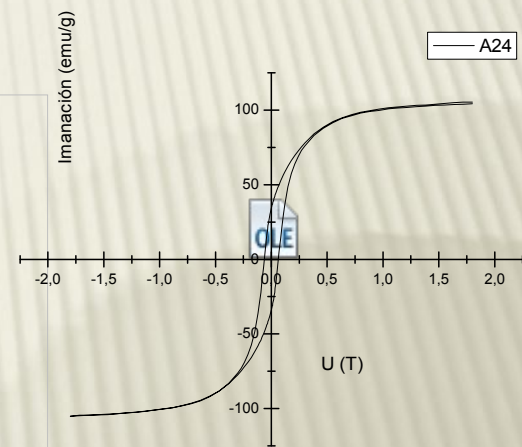
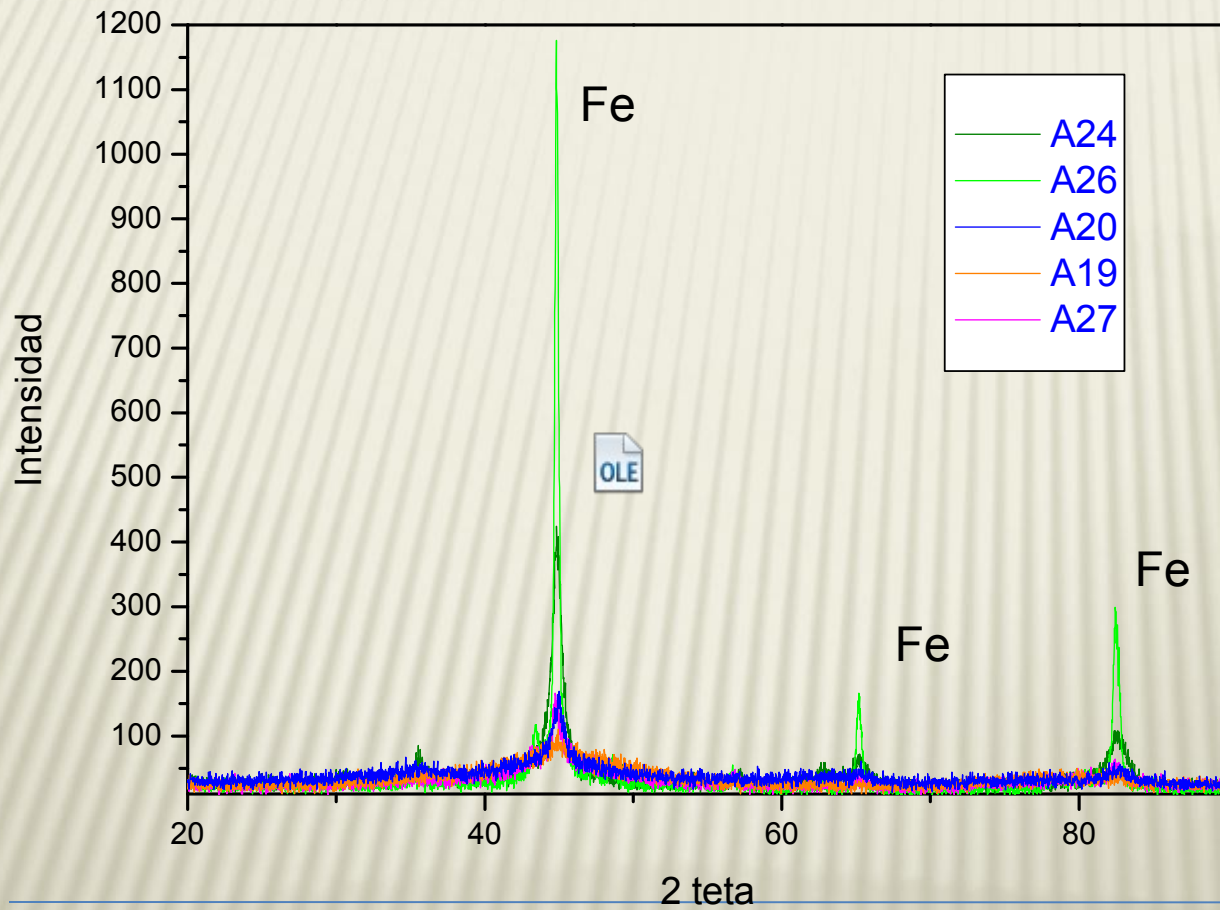


$MS=127,55 \text{ emu} \cdot \text{g}^{-1}$

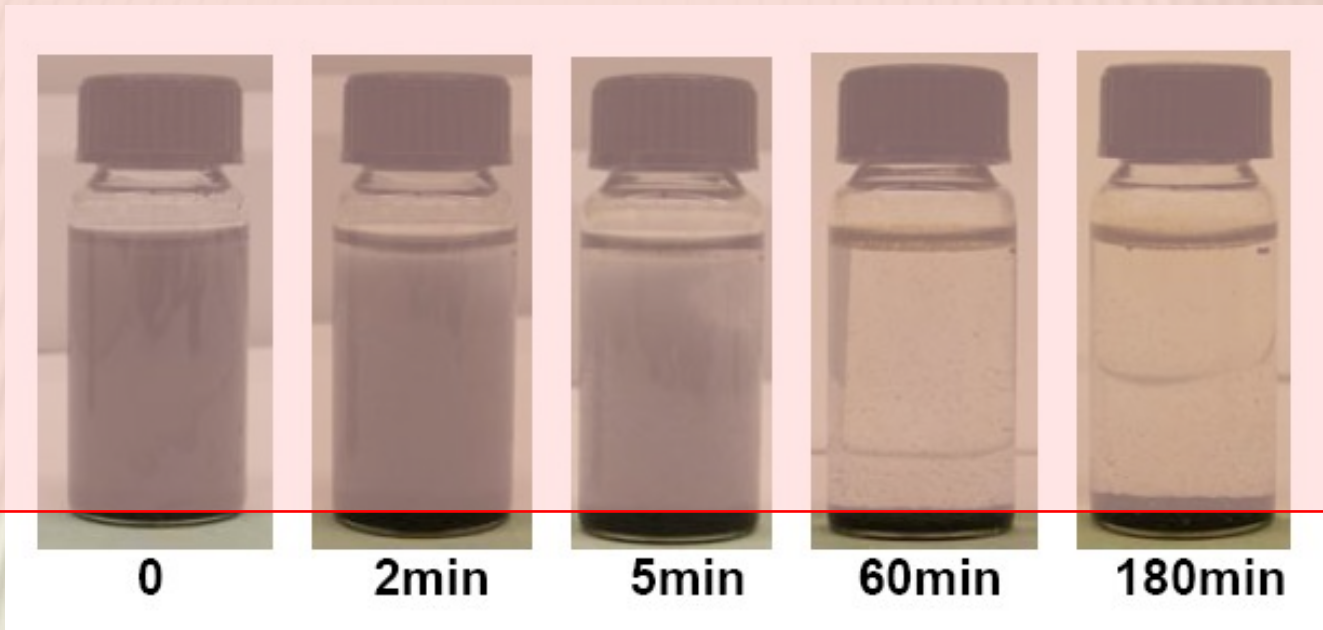
Muestra	Tamañ. (nm)	Agit. (rpm)	Iny. (min)	Relación (FeCl ₂ /NaBH ₄)	Ms (emu*g ⁻¹)
A 32	99	500	3,25	1:8	116,23
A 33	86	500	3,03	1:8	110,24
A35	83	500	2,28	1:3	136,24
A 36	40	500	3,92	1:6	122,09
A 37	78	500	3,22	1:4	131,79
A 38	71	500	3,45	1:5	127,55
A 39	66	500	3,08	1:7	121,24

SYNTHESIS OF nZVI

DRX



❖ Stability



CASI CONCLUYENDO...

Se han establecido los parámetros críticos de la síntesis y se han ajustado

Se han sintetizado partículas de unas características determinadas, de manera reproducible

Se ha logrado eliminar la agregación en forma de collares.

Se ha conseguido una mayor dispersión. Las partículas ya no se agregan durante la síntesis sino que están unidas electrostáticamente.

TYPE AND CONCENTRATION OF STABILIZERS

Para evitar la agregación y la oxidación:

- ❖ **PAA (poliácido acrílico)**: polielectrolito aniónico ($M_w = 50000$)
- ❖ **PEG (polietilen glicol)**: ($M_n = 1000$)
- ❖ **CMC (Carboximetil celulosa)**
- ❖ **PVA (polialcohol vinílico)**

Biodegradables, biocompatibles, solubles en agua

Methods of synthesis

1.- Stabilization in-situ:

There is only one step

The nanoparticles are synthesized with the polymer:



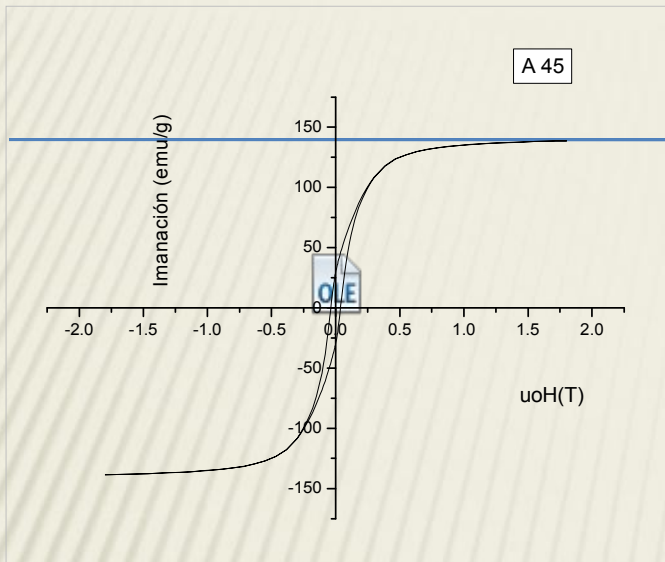
2.- Post-stabilization:

There are two steps

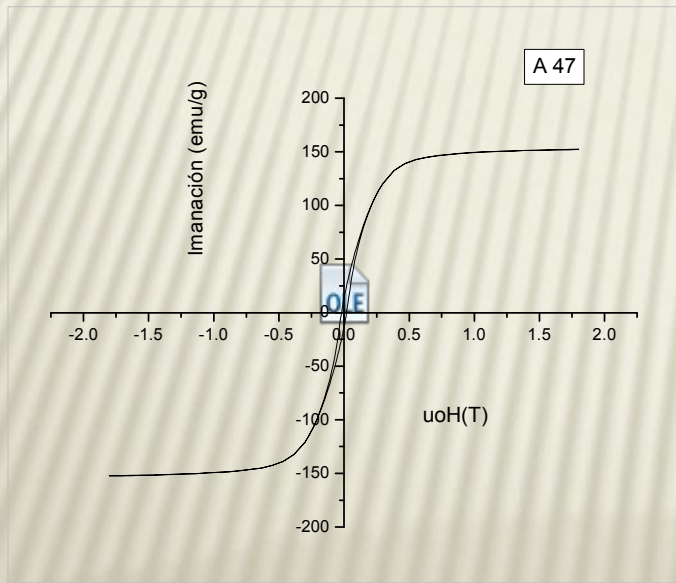
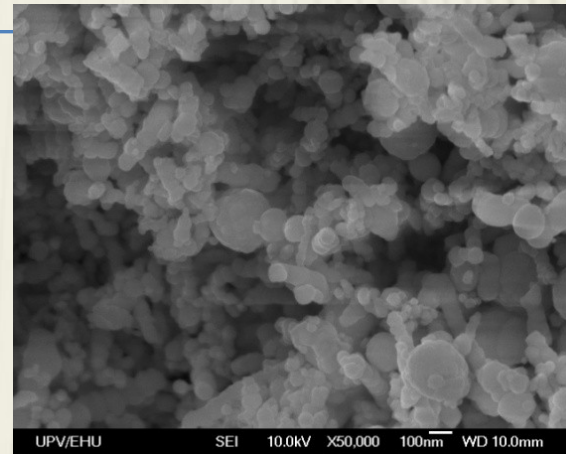


SYNTHESIS OF STABILIZED nZVI : PAA, PEG

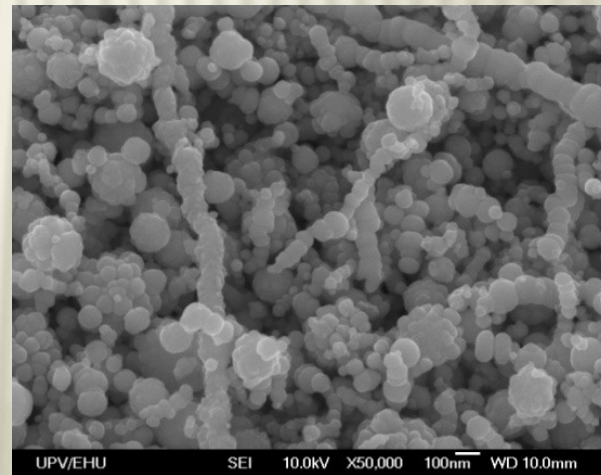
Muestra	Agitac. (rpm)	t. Iny. (min)	[FeCl ₂] (M)	[NaBH ₄] (M)	Polím.	t. Reacc. (min)	Ms (emu*g ⁻¹)
(Pre) A 40	500	3,05	0,03	0,2	PAA(0,5%)	60	86,95
(Pre) A 41	500	3,38	0,03	0,2	PAA(0,5%)	30	123,28
(Pre) A 42	500	3,22	0,03	0,2	PAA (1%)	30	124,31
(Pre) A 43	500	3,1	0,06	0,2	PAA(0,5%)	30	126,52
(Sim) A 44	500	3,16	0,03	0,2	PAA(0,5%)	30	98,98
(Post) A 45	500	3,23	0,03	0,2	PAA(0,5%)	30	138,59
(Pre) A 46	500	3,12	0,03	0,2	PEG (0,5%)	30	130,52
(Post) A 47	500	3,1	0,03	0,2	PEG (0,5%)	30	152,38



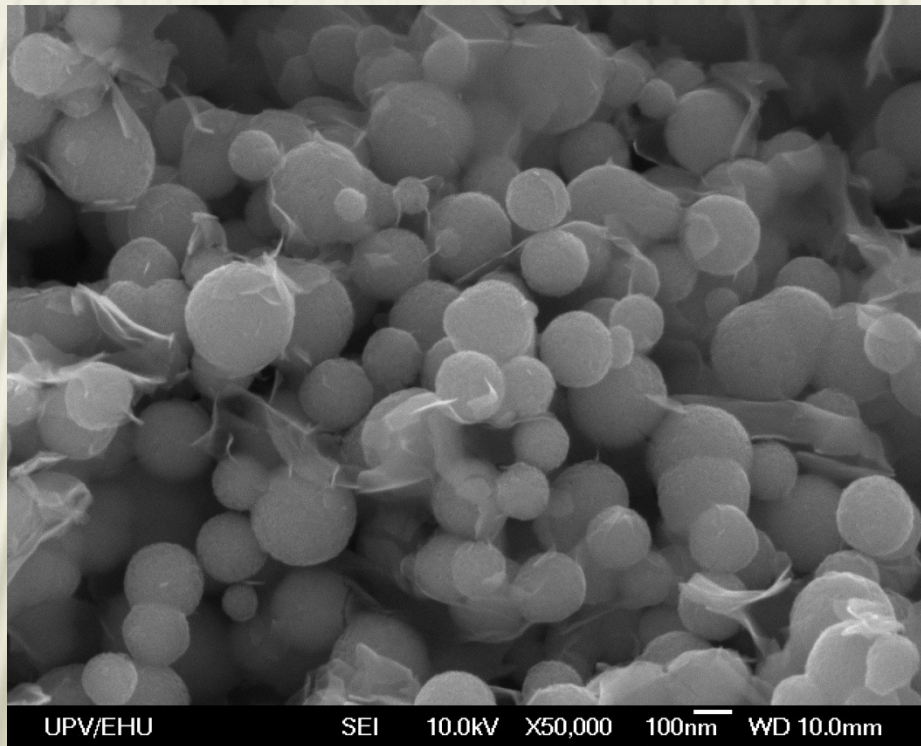
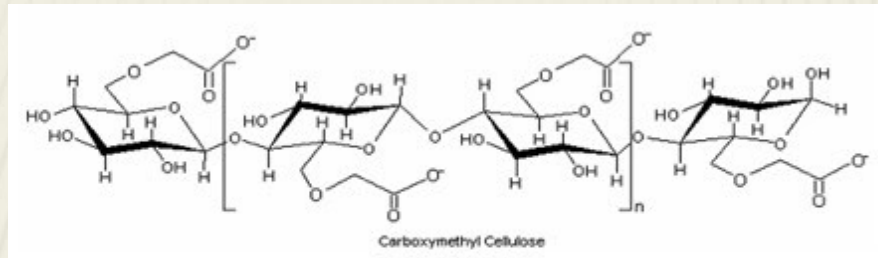
A45 Post (PAA)



A47 Post (PEG)



CARBOXIMETIL CELULOOSA (CMC)



REACTIVITY

- × Procedimiento PE.CM:LQ-05-E: *Procedimiento de ensayo para la determinación de cromo total y cromo hexavalente disueltos en agua por el método colorimétrico de la difenilcarbazida.*

$$\% \text{ reactividad} = \frac{[\text{Cr(VI)}]_0 - [\text{Cr(VI)}]}{[\text{Cr(VI)}]_0} \times 100$$

$[\text{Cr(VI)}]_0$: concentración de Cromo (VI) inicial,

$[\text{Cr(VI)}]$: concentración de Cr(VI) después de la reacción con las nZVI]

La $[\text{Cr(VI)}]_0$ empleada es de 500mg/

REACTIVITY

Muestra	Atm.	Lav.(H2O)	Iny.	Agit. (rpm)	Iny. (min)	Reactividad % Cr (VI)
A 57	aire	1	FeCl ₂	500	3	44
A 58	aire	1	Na BH ₄	500	3	46
A 59	N2	1	FeCl ₂	500	2	71
A 61	aire	0	FeCl ₂	500	2	41
A 62	N2	0	FeCl ₂	500	3	69
A 63	aire	0	Na BH ₄	500	3	43

REACTIVITY

Muestra	[Fe(0)] (M)	Atm.	Tiempo reacción (min)	Lavados	Reactividad (%) Cr(VI)
19.01.11	5	argon	5	3	94
24.01.11	5	argon	5	3	80
8.03.11	5	argon	5	3	56
8.03.11	5	argon	5	3	65
8.02.11	5	argon	5	3	53
8.02.11	5	argon	5	3	50
9.02.11	5	argon	5	3	58
14.02.11	5	argon	30	3	53
17.02.11	5	argon	90	3	63
8.02.11	5	argon	5	0	73
9.02.11	5	argon	5	1	72

REACTIVITY $n\text{Fe(0)}+\text{PAA}$

MUESTRA	ATM.	L (H_2O)	AG. (rpm)	PAA (ml)	Fe (g)	REACT. % Cr(VI)
A 65 _{PRE}	aire	1	500	1	0,5024	42
A 66 _{POST}	aire	1	500	1	0,5045	40
A 67 _{PRE}	aire	1	500	1	0,5011	50
A 68 _{POST}	aire	1	500	1	0,5029	51
A 69 _{PRE}	N2	1	500	1	0,5031	49
A 70 _{POST}	N2	1	500	1	0,5026	56
A 71 _{PRE}	N2	1	500	1	0,5298	69
A72 _{POST}	N2	1	500	1	0,5010	82

REACTIVITY nFE(0) + CMC

MUESTRA	Método	ATM.	[CMC]: [FeCl₂]	[Fe (0)] (M)	Ultrasonicada s	REACT. % Cr(VI)
26/04/11	Pre-aglomeración	argon	0,06	5	No	65
28/04/11	Pre-aglomeración	argon	0,06	5	Sí	65
02/05/11	Pre-aglomeración	argon	0,06	5	Sí	72
25/05/11	Pre-aglomeración	argon	0,11	5	Sí	60
25/05/11	Pre-aglomeración	argon	0,11	5	Sí	59
24/05/11	Pre-aglomeración	argon	0,11	5	Sí	88

nZVI stabilized with CMC



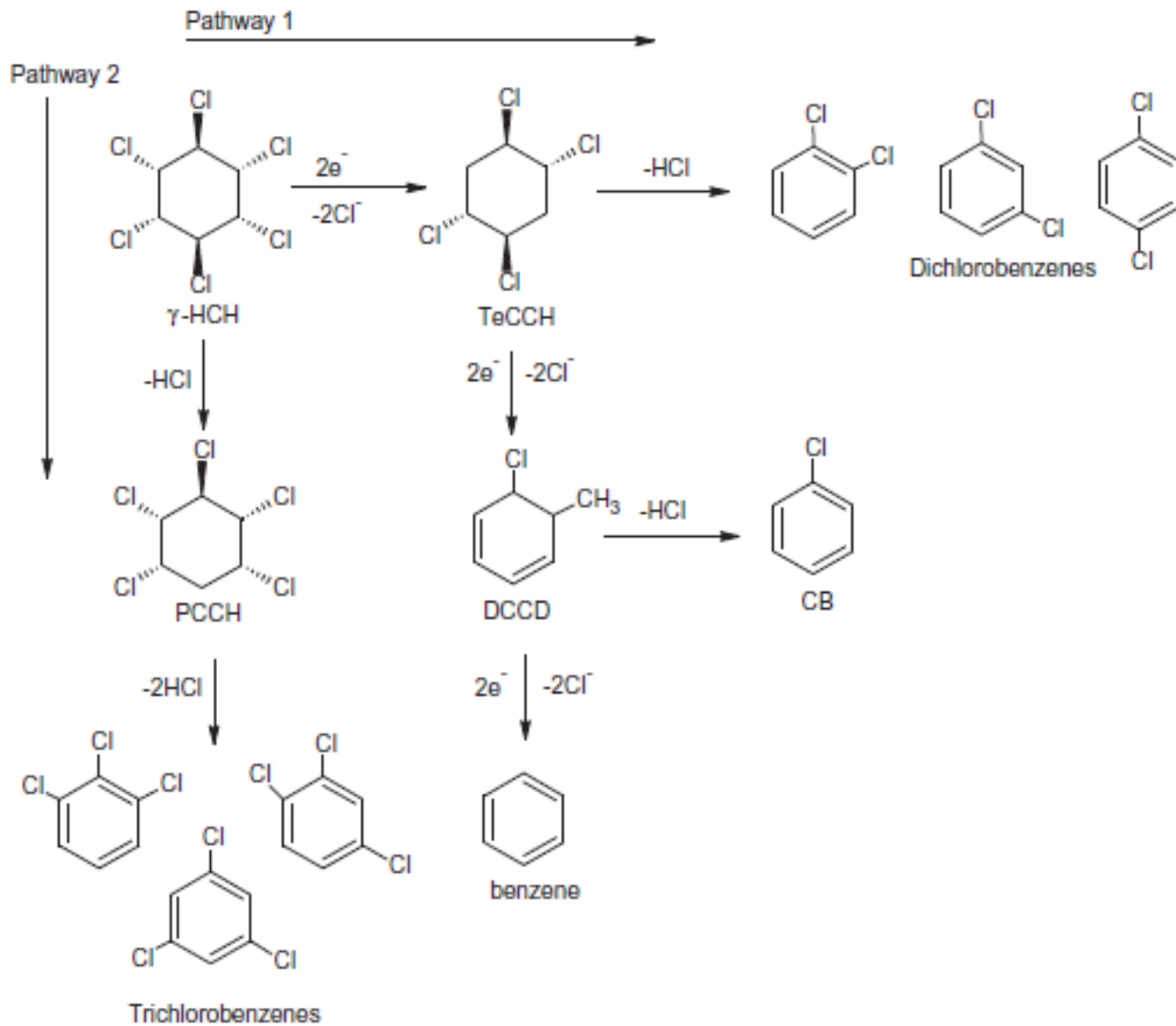
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2min

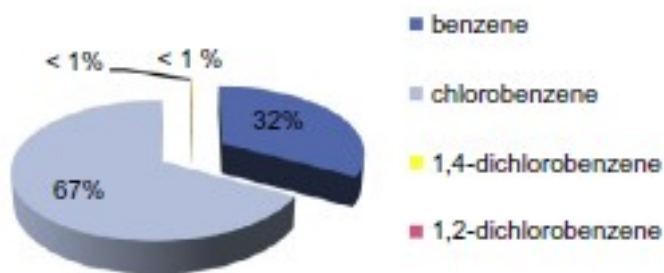
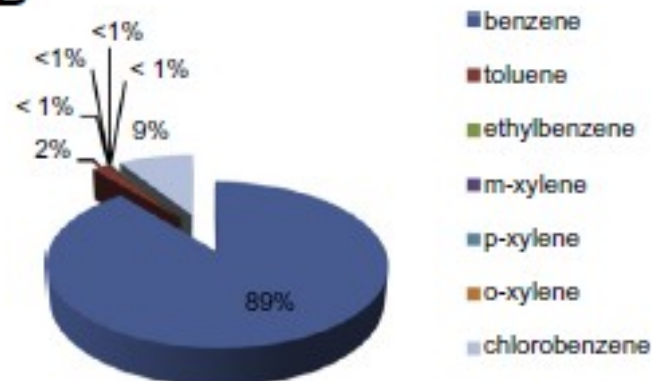
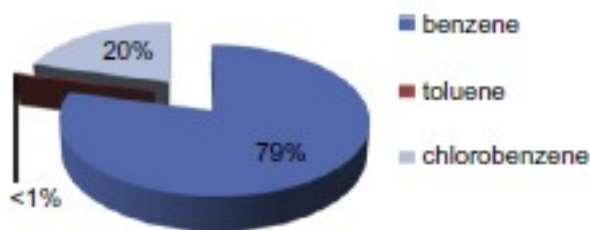
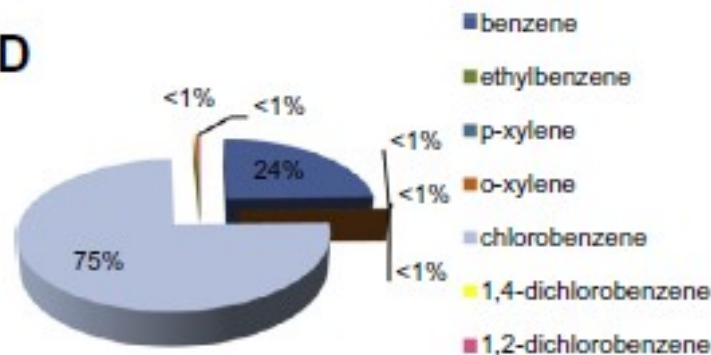
5min

60min

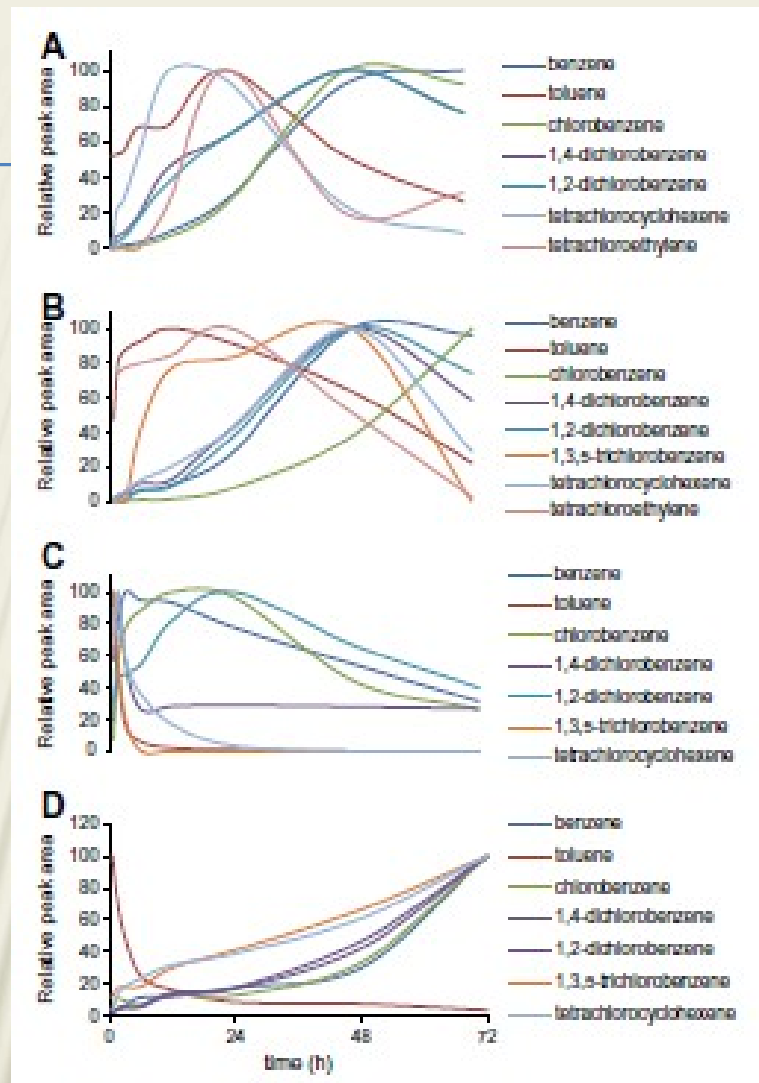
20days



Possible pathways of lindane degradation in the presence of NZVI
 Chemosphere 93 (2013) 1324–1332

A**B****C****D**

Identified volatile compounds in four lindane water samples treated with different nanoiron particles once the degradation reaction have been completed: (A) uncoated iron nanoparticles; (B) nanoiron particles coated with PAA; (C) nanoiron particles coated with PAP; and (D) nanoiron particles coated with CMC. The percentages were calculated taken into account the relative peak area respect to the total peak area for each sample.

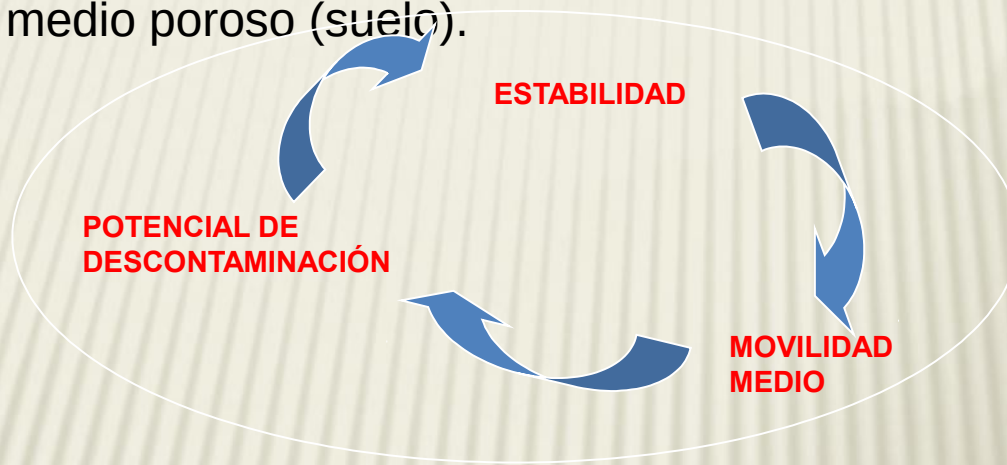


Identified volatile compounds and their evolution in the headspace with time of four lindane water samples treated with different types of iron nanoparticles: (A) uncoated iron nanoparticles; (B) nanoiron particles coated with PAA; (C) nanoiron particles coated with PAP; and (D) nanoiron particles coated with CMC. The relative peak areas were calculated taken into account the relative peak area respect to the total peak area of each analyte.

SOIL REMEDIATION: OBJETIVES

La formulación del producto a desarrollar debe alcanzar un equilibrio entre el potencial de descontaminación de la nanopartícula sobre el/los contaminante(s) y su

Movilidad en el medio poroso (suelo).



Puntos de avance claves:

- ❖ Optimizar el proceso de estabilización
- ❖ Optimizar la reactividad de la nanopartícula
- ❖ Optimizar la movilidad de las nanopartículas en el medio poroso

Acabando...

El control de diferentes parámetros permite la síntesis de nanopartículas que son, aproximadamente, esféricas y que, como se ha indicado, presentan una amplia distribución de tamaños.

El mayor efecto sobre el tamaño de las nanopartículas es consecuencia de la concentración de las especies presentes en la mezcla de reacción, existiendo un límite en el que aparecen partículas de menor tamaño con agregados grandes de pequeñas partículas (80nm).

Se han determinado los parámetros críticos de la síntesis y el ajuste de éstos permitiendo la síntesis de nanopartículas estables de unas características determinadas y de manera reproducible (a medida).

Del estudio de la eficacia (reactividad) del nanohierro, se han obtenido valores elevados de la capacidad descontaminante del material frente a algunas sustancias peligrosas habituales.

TECHNICAL CONSTRAINTS AND FUTURE RESEARCH NEEDS

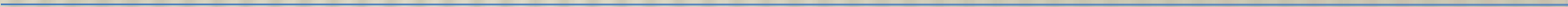
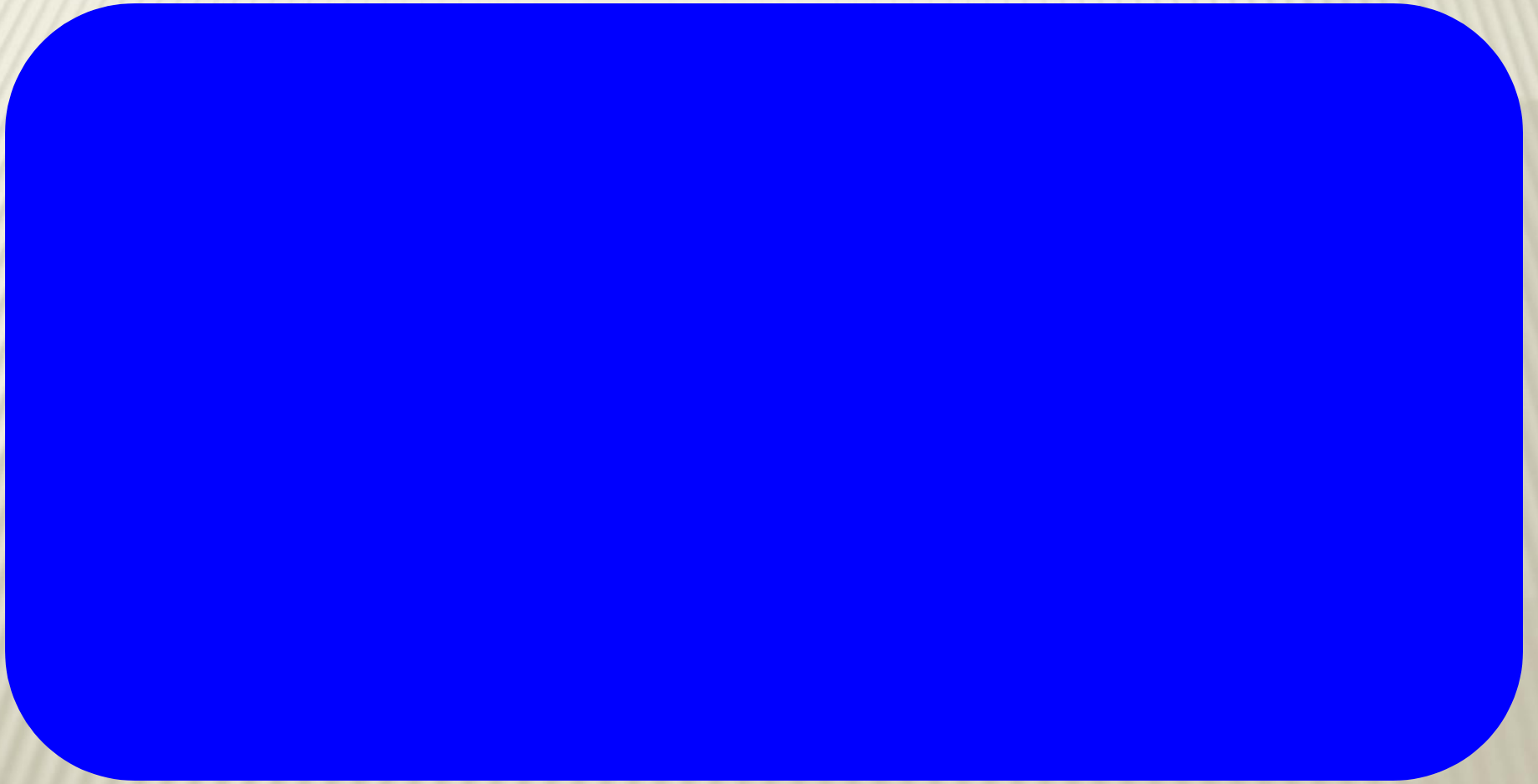
Although the particle stabilization technique (especially the use of CMC) has greatly improved the soil deliverability of nZVI, the transport distance remains a bottle neck for effective application of the technology, especially for soil of low permeability

It has been challenging to extend the reactive lifetime of nZVI.

Further studies are needed to investigate how delivered nZVI affects the biogeochemical conditions and mobility of other chemicals in the subsurface

There is a need to further study the synergistic or antagonistic effects of nZVI and microbial activities

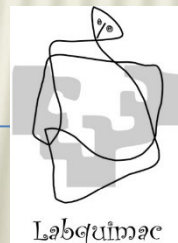
Futuro ...





NANOTECHNOLOGY AS A TOOL FOR SOIL RECOVERY

ESKERRIK ASKO, THANK YOU, GRACIAS



José Luis Vilas Vilela

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