Membrane-Based Nanostructured Metals for Reductive Degradation of Hazardous Organics at Room Temperature

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Functionalized Materials and Membranes (Nano-domain Interactions)

Ultra-High Capacity Metal Sorption (Hg, Pb etc)

Bhattacharyya, Hestekin, et al, J. Memb. Sci. (1998)
Ritchie, Bachas, Sikdar, and Bhattacharyya, LANGMUIR (1999)
Ritchie, Bachas,Sikdar, and Bhattacharyya, ES&T (2001)

Reactions and Catalysis (nanosized metals, Vitamin B12, Enzymes)

Tunable Separations (with Polypeptides)

Hollman and Bhattacharyya, LANGMUIR (2002,2004); JMS (2004)
Smuleac, Butterfield, Bhattacharyya, Chem. of Materials (2004)

*Ahuja, Bachas, and Bhattacharyya, I&EC (2004)

Why Nanoparticles?

- High Surface Area
- Significant reduction in materials usage
- Reactivity (role of surface defects, role of dopants such as, Ni/Pd)
- Polymer surface coating to alter pollutant partitioning
- Alteration of reaction pathway (ex, TCE --→ ethane)
- Bimetallic (role of catalysis and hydrogenation, minimizing surface passivation)
- Enhanced particle transport in groundwater

Synthesis of Metal Nanoparticles in Membranes and Polymers

- **Chelation (use of polypeptides,poly(acids), and polyethyleneimine)**
  - Capture and borohydride reduction of metal ions using polymer films containing **polyfunctional** ligands.

- Mixed Matrix Cellulose Acetate Membranes
  - Incorporation of metallic salts in membrane casting solutions for dense film preparation. Formation of particles within the membrane occurs after film formation.
  - External Nanoparticle synthesis followed by membrane casting

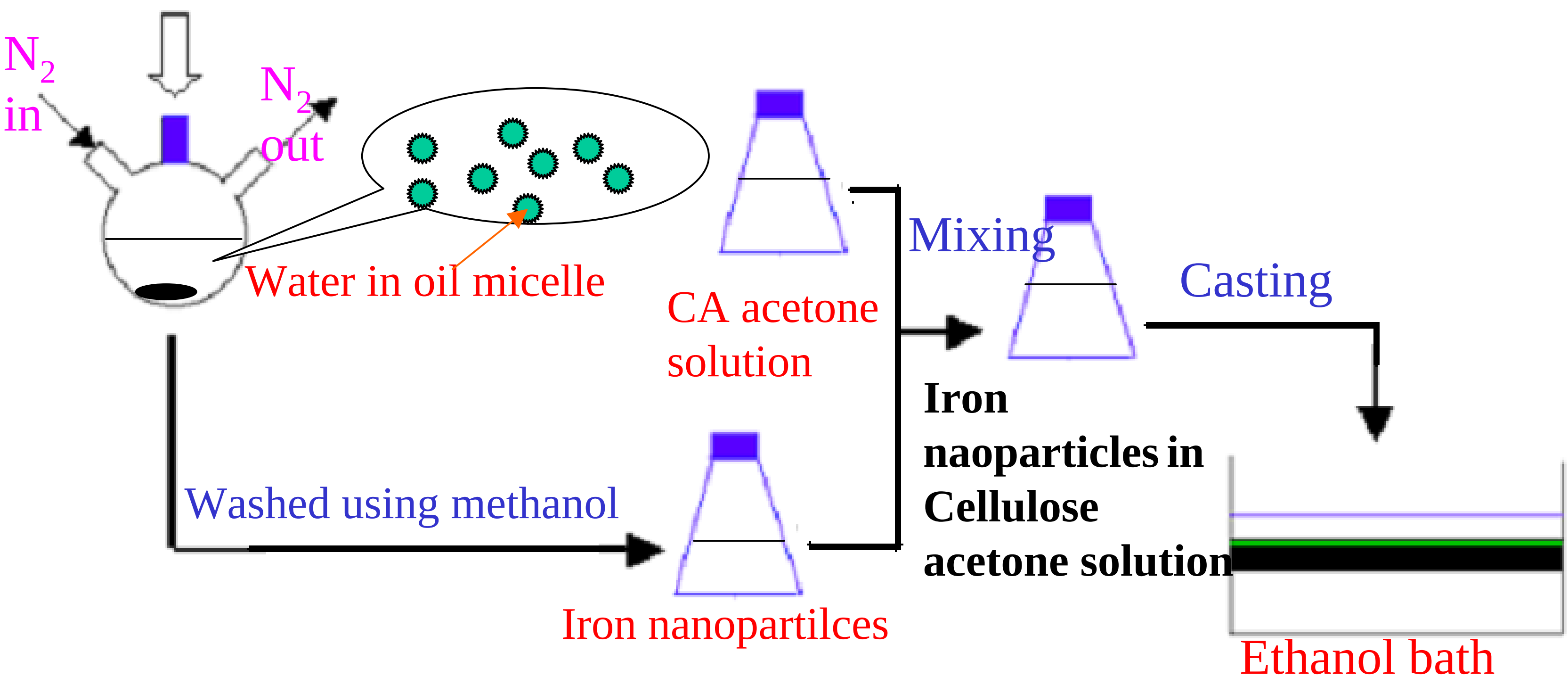
- **Thermolysis and Sonication**
  - Controlled growth of metal particles in polymeric matrices by decomposition of metal carbonyl compounds thermally or by sonication.

- **Di-Block Copolymers**
  - The use of block copolymers containing metal-interacting hydrophilic and hydrophobic segments provide a novel approach for in-situ creation of nanostructured metals (4-5 nm)

Preparation of supported iron nanoparticles

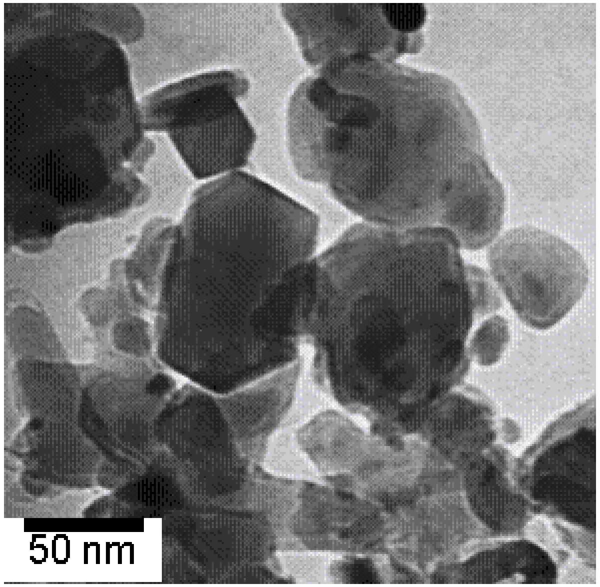
❖**Synthesis reaction:** $2FeCl_3 + 6NaBH_4 + 18H_2O \longrightarrow$

$2Fe(s) + 21H_2(gas) + 6B(OH)_3 + 6NaCl$

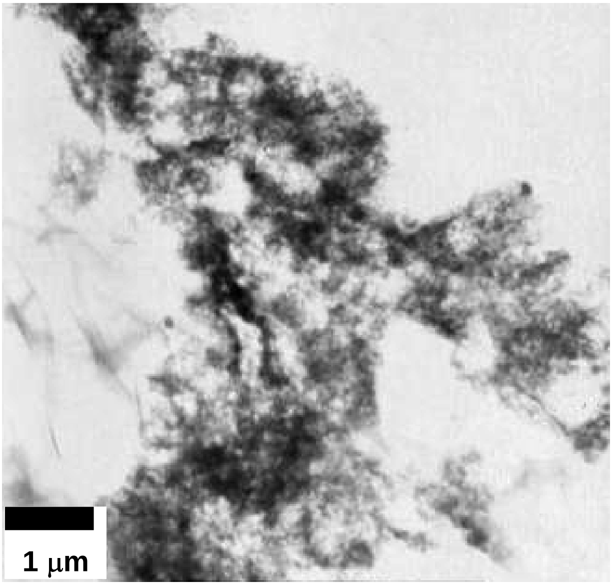


❖ **The weight content of iron is 6.6% by AA (Atomic Absorption).**

TEM Characterization of pre-produced iron particles

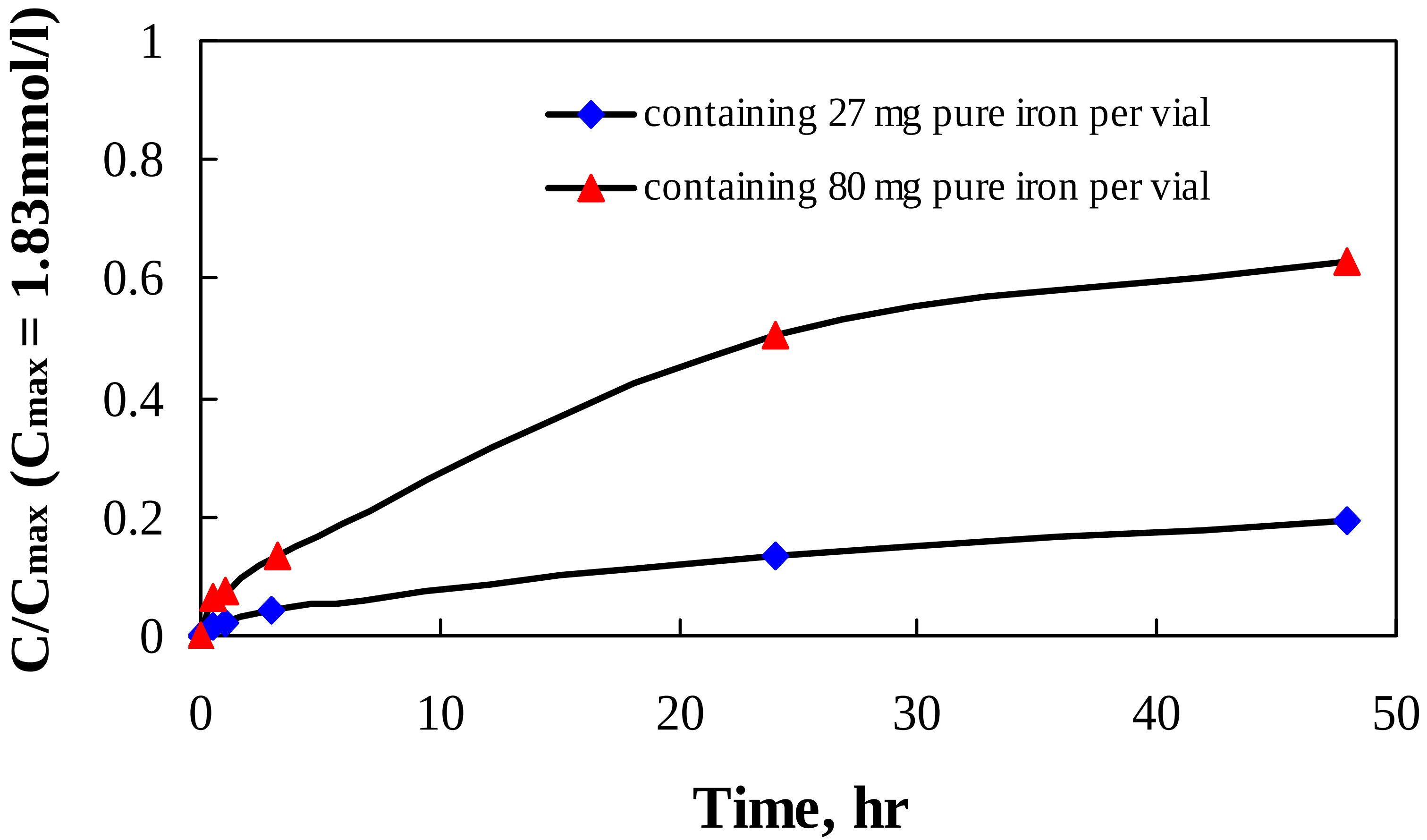


❖TEM bright field image of pre-produced iron particles

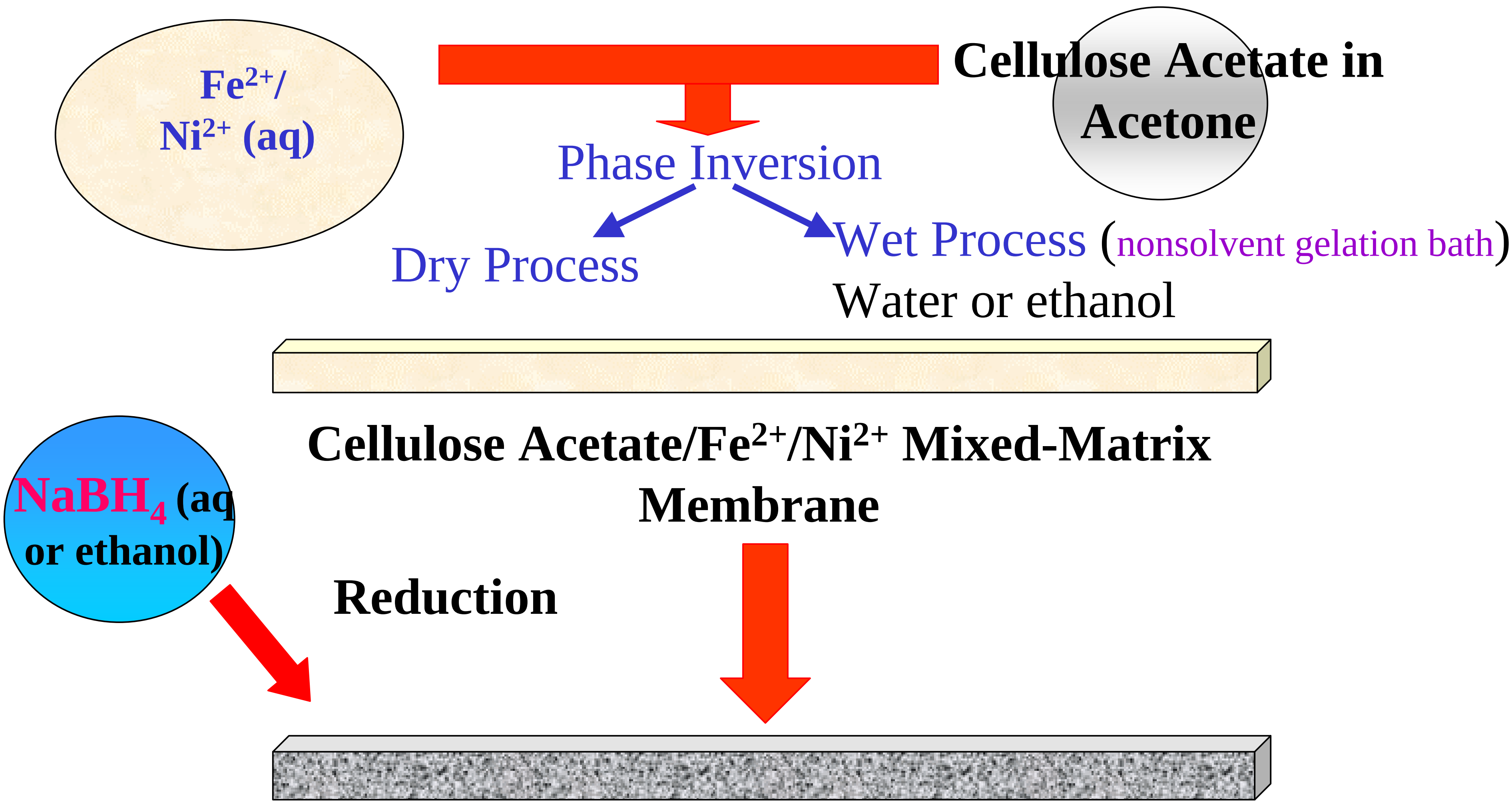


❖TEM bright field image of CA membrane-supported iron nanoparticles

Change of chloride ions in aqueous phase (TCE degradation to Cl^-)

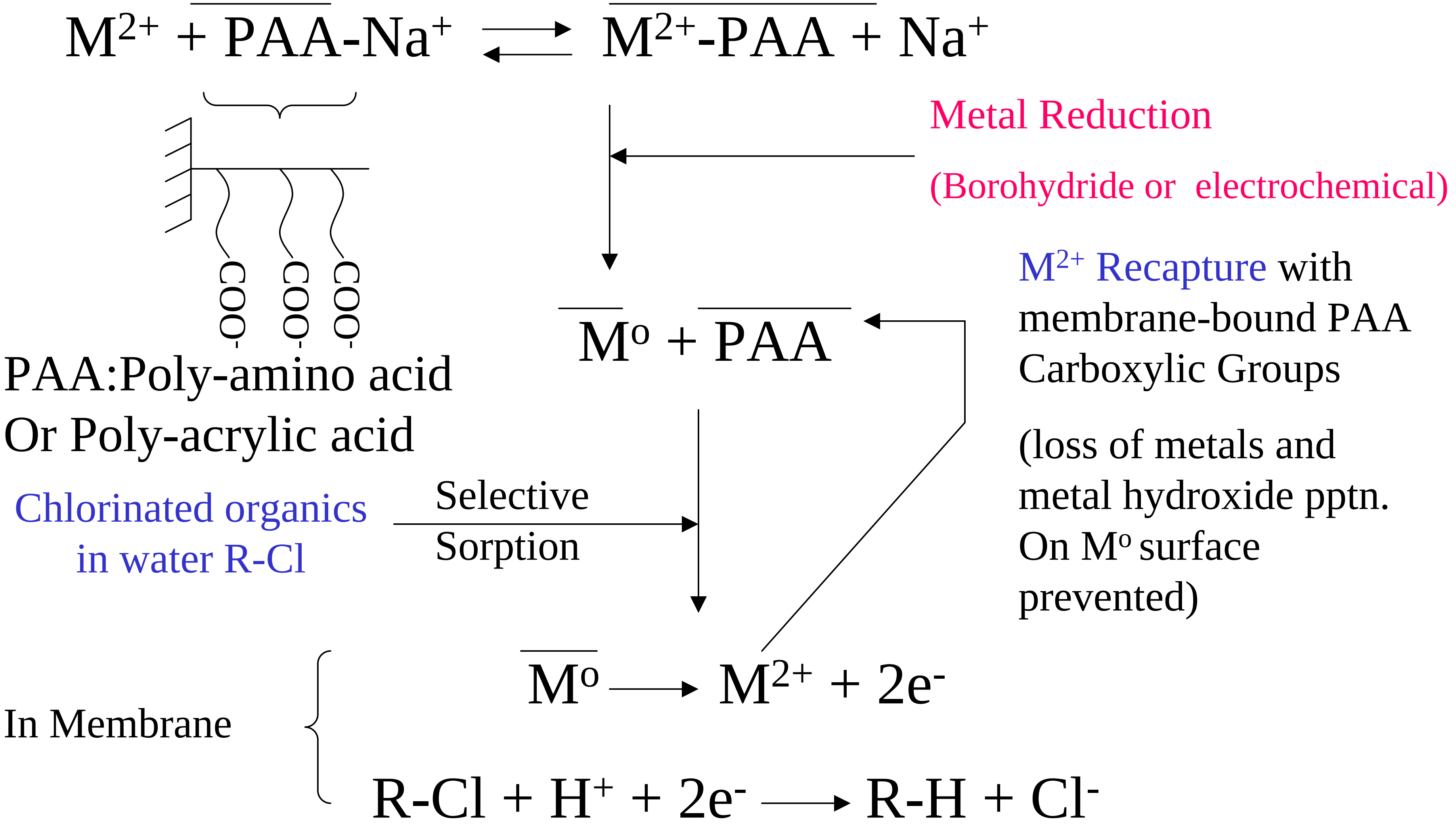


Mixed-Matrix Membrane Preparation



Cellulose Acetate/Nanoscale Fe-Ni Mixed-Matrix Membrane

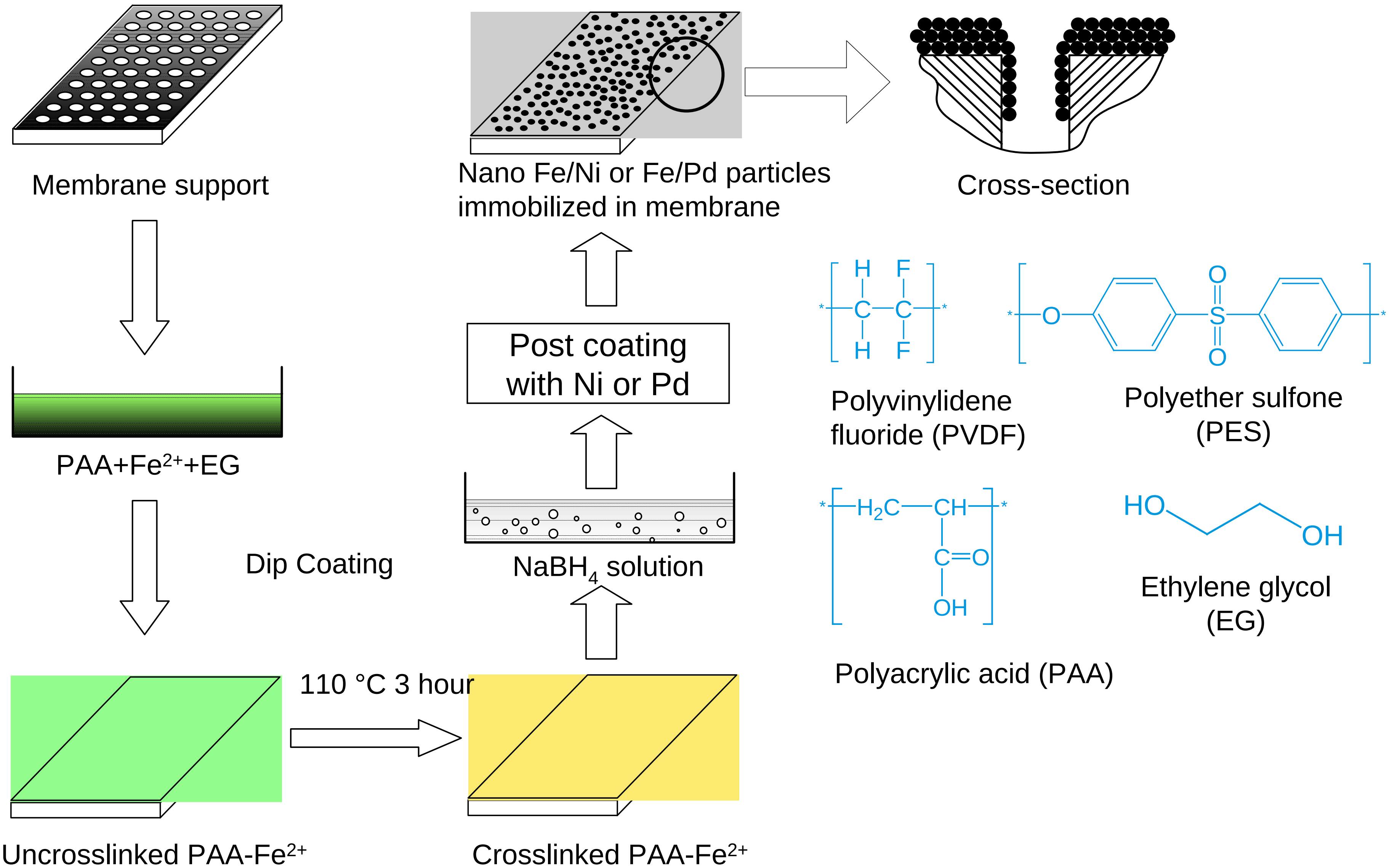
Meyer, Bachas, and Bhattacharyya, Env. Prog (2004)

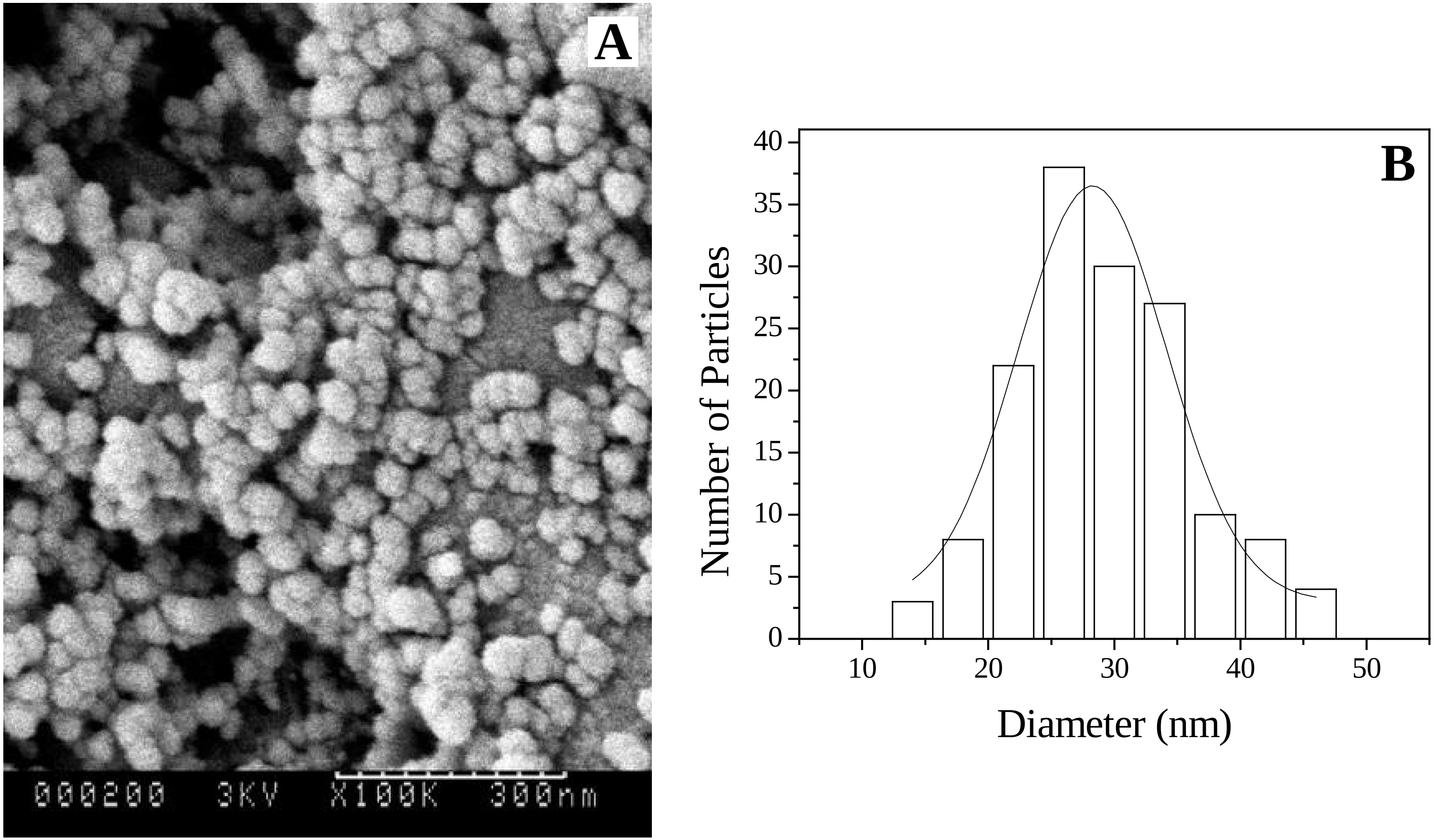


$\overline{M^{o}}$: Nanosized M^{o} in membrane phase

Nano-structured Metal Formation and Hazardous Organic Dechlorination with Functionalized Membranes (with simultaneous recapture/reuse of dissolved metals).

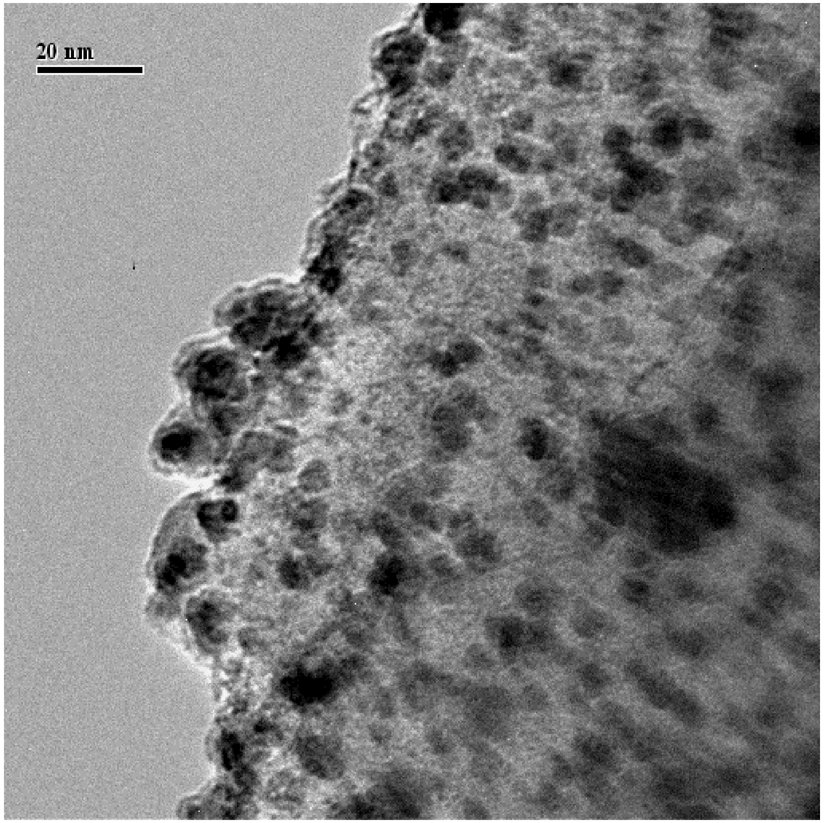
Nanoparticle Synthesis in Membrane (use of PAA)

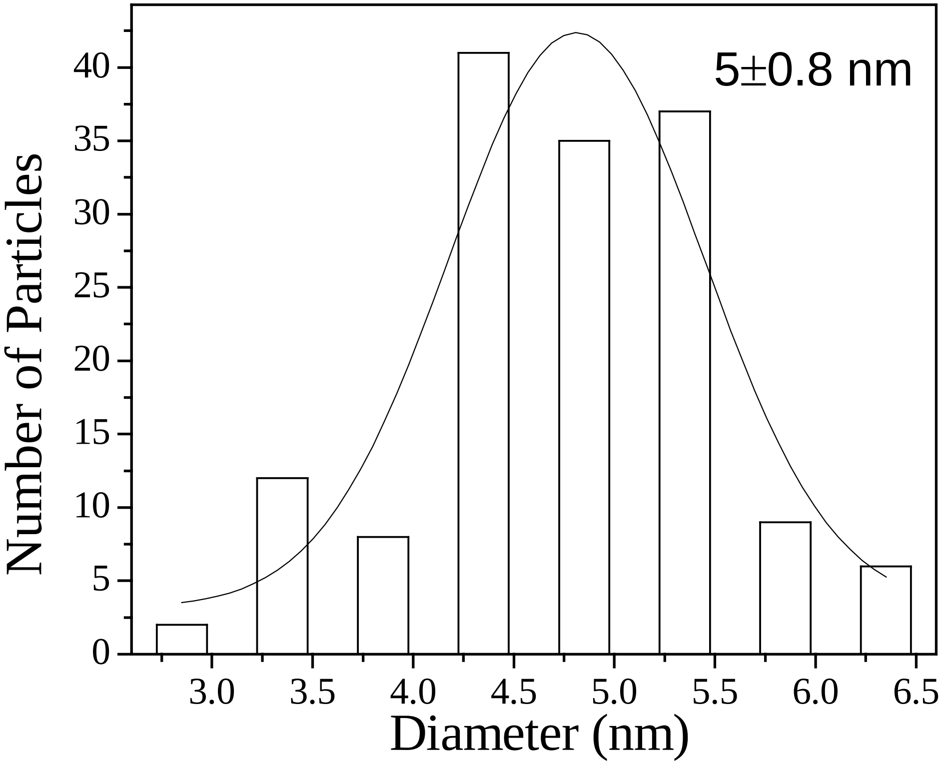




(A) SEM surface image of nanoscale Fe/M particles immobilized in PAA/MF composite membrane (reducing Fe followed by metal deposition) (100,000×); (B) Histogram from the left SEM image of 150 nanoparticles. The average particle size is 28 nm, with the size distribution standard deviation of 7 nm.

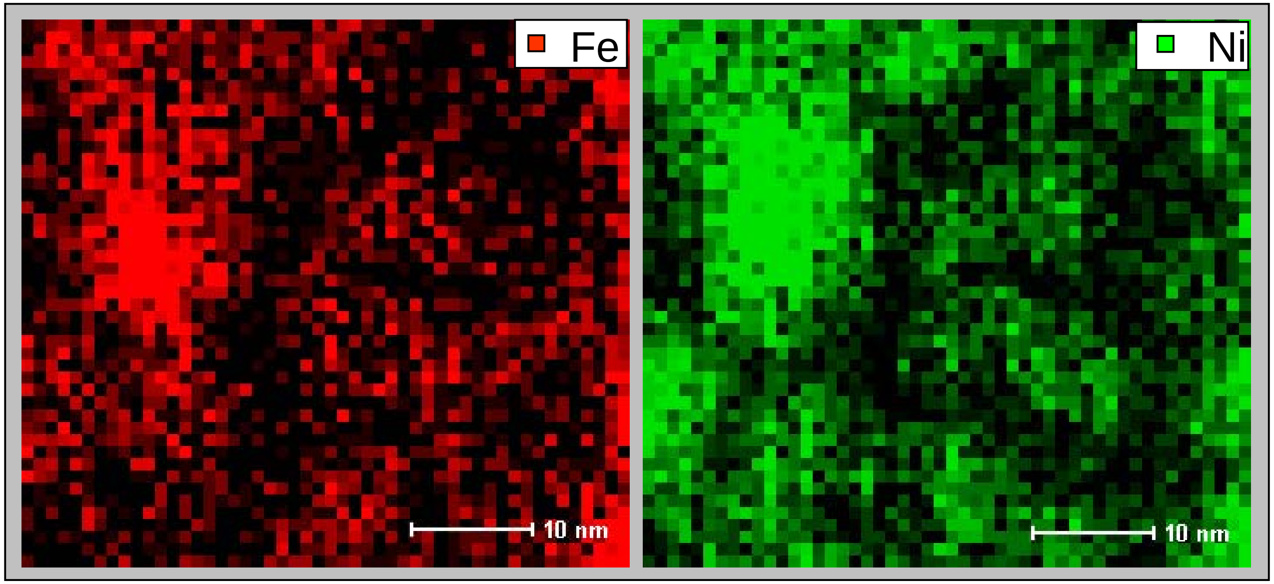
Image of Fe/Ni particles Prepared in a TEM Grid (Ni post-Coated)



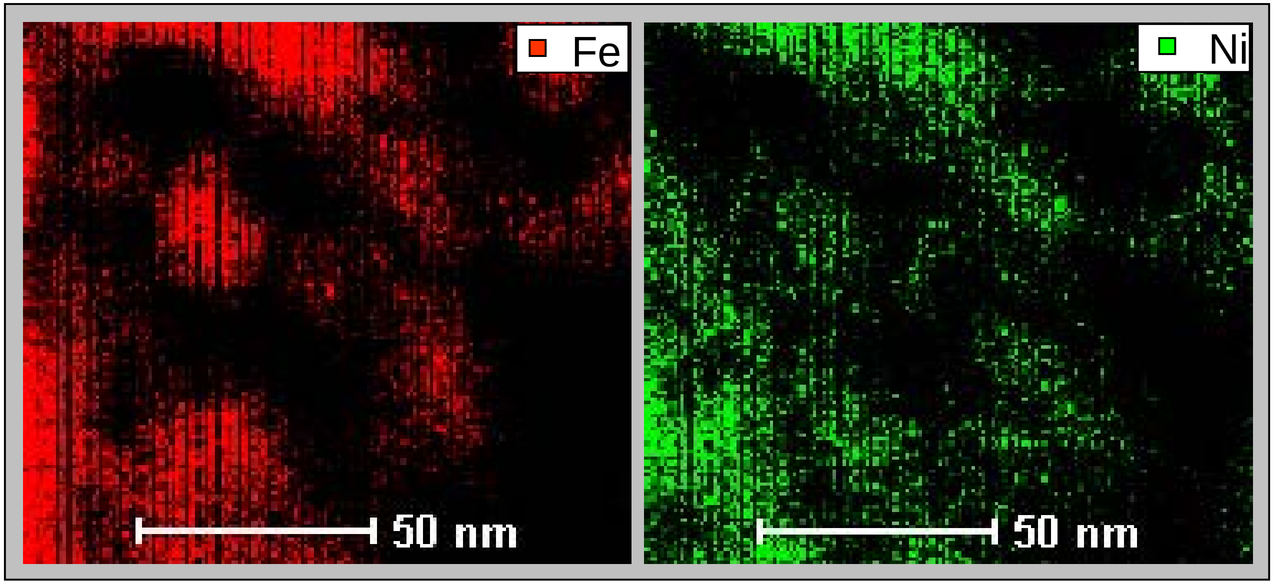


STEM-EDS Mapping (using JOEL 2010)

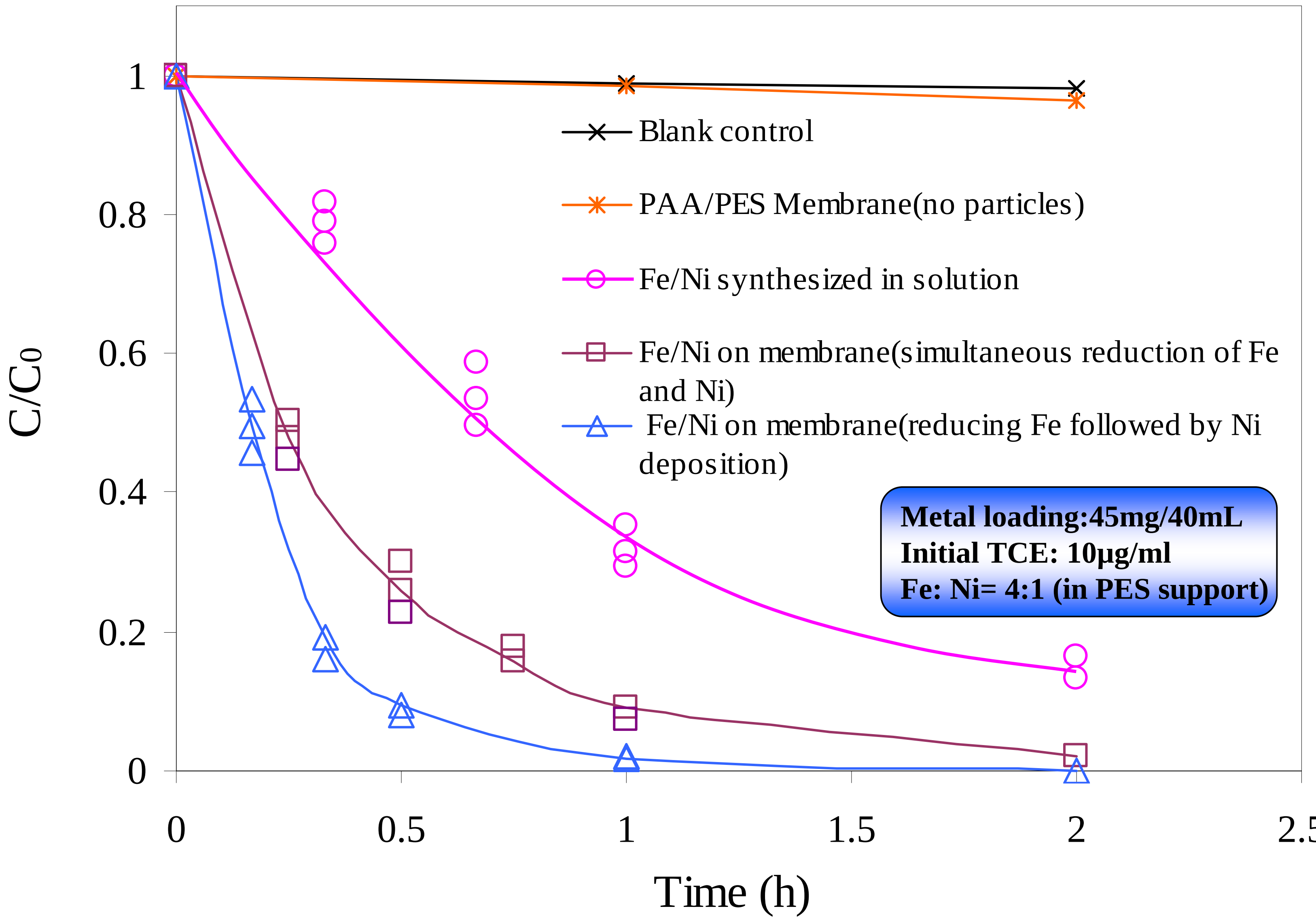
Reducing Fe followed by Ni deposition



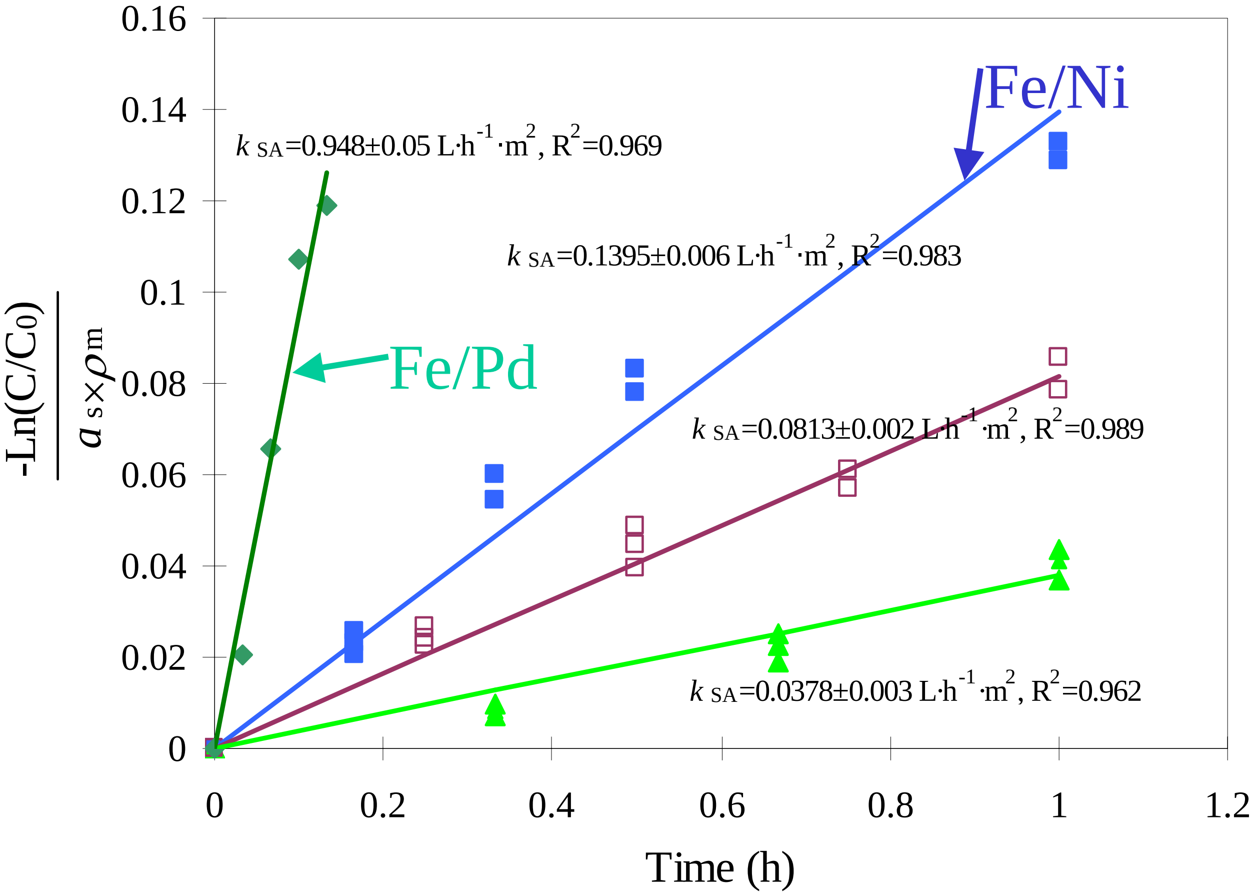
Simultaneous reduction of Fe and Ni



TCE Dechlorination by Fe/Ni and Fe/Pd Nanoparticles in Membrane



Surface-Area-Normalized Dechlorination Rate (wide variation of k_{SA} showing the importance of surface – active sites and role of hydrogenation)



(□)Fe/Ni (simultaneous reduction);
(■)Fe/Ni (Ni deposition on Fe);
(▲)Fe/Ni (solution phase)
(◆) Fe/Pd

$$\frac{dC}{dt} = -k_{SA} a_s \rho_m C$$

C: TCE concentration

k_{SA}: surface-area-normalized reaction rate

a_s: specific surface area

ρ_m: *mass concentration of metal*

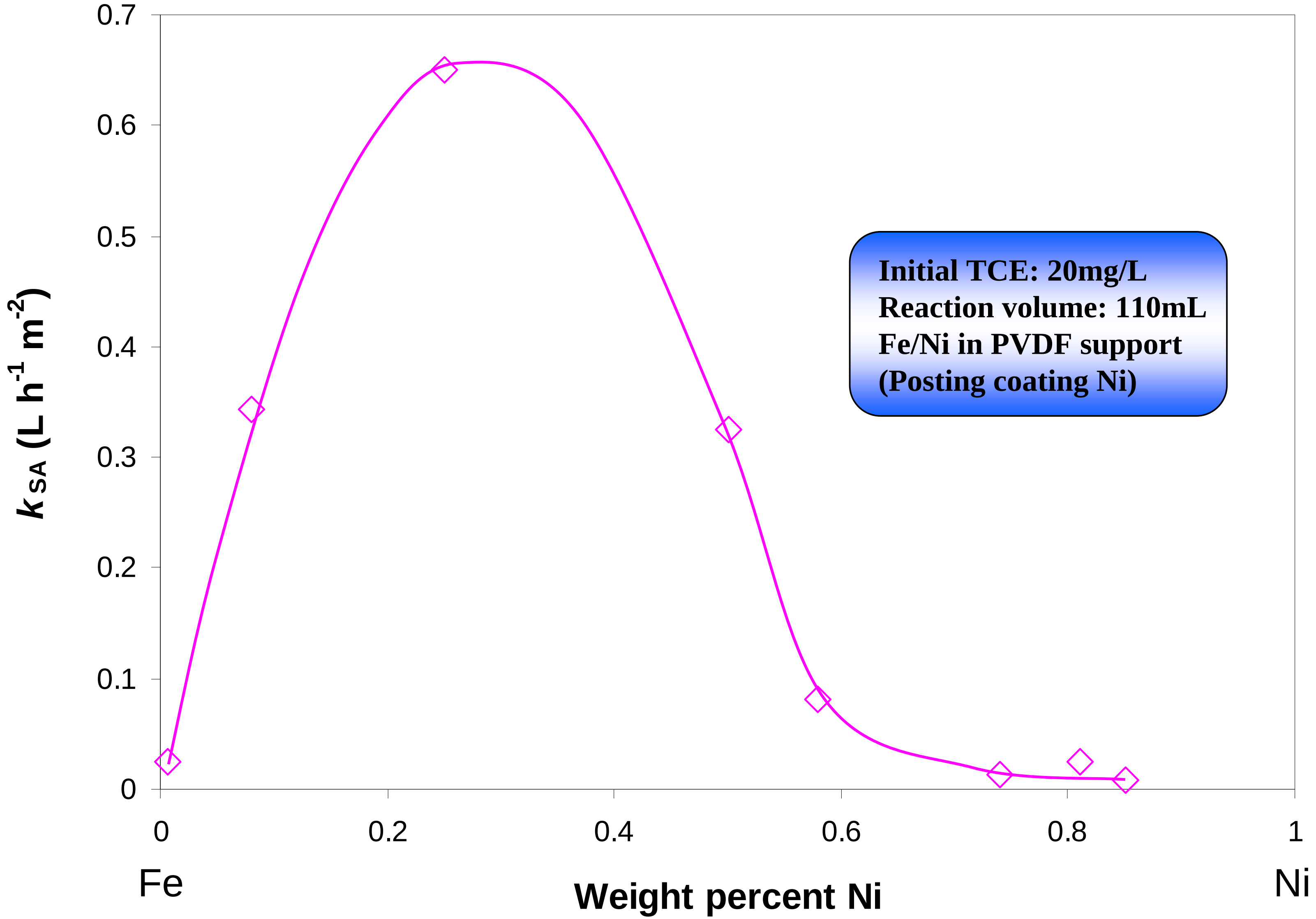
t: time

Other source k_{SA}*

Material	K_{SA} (L·h^{-1}·m^2)
Nano Fe	2.0×10^{-3}
Nano Fe/Ni (3:1)	0.098

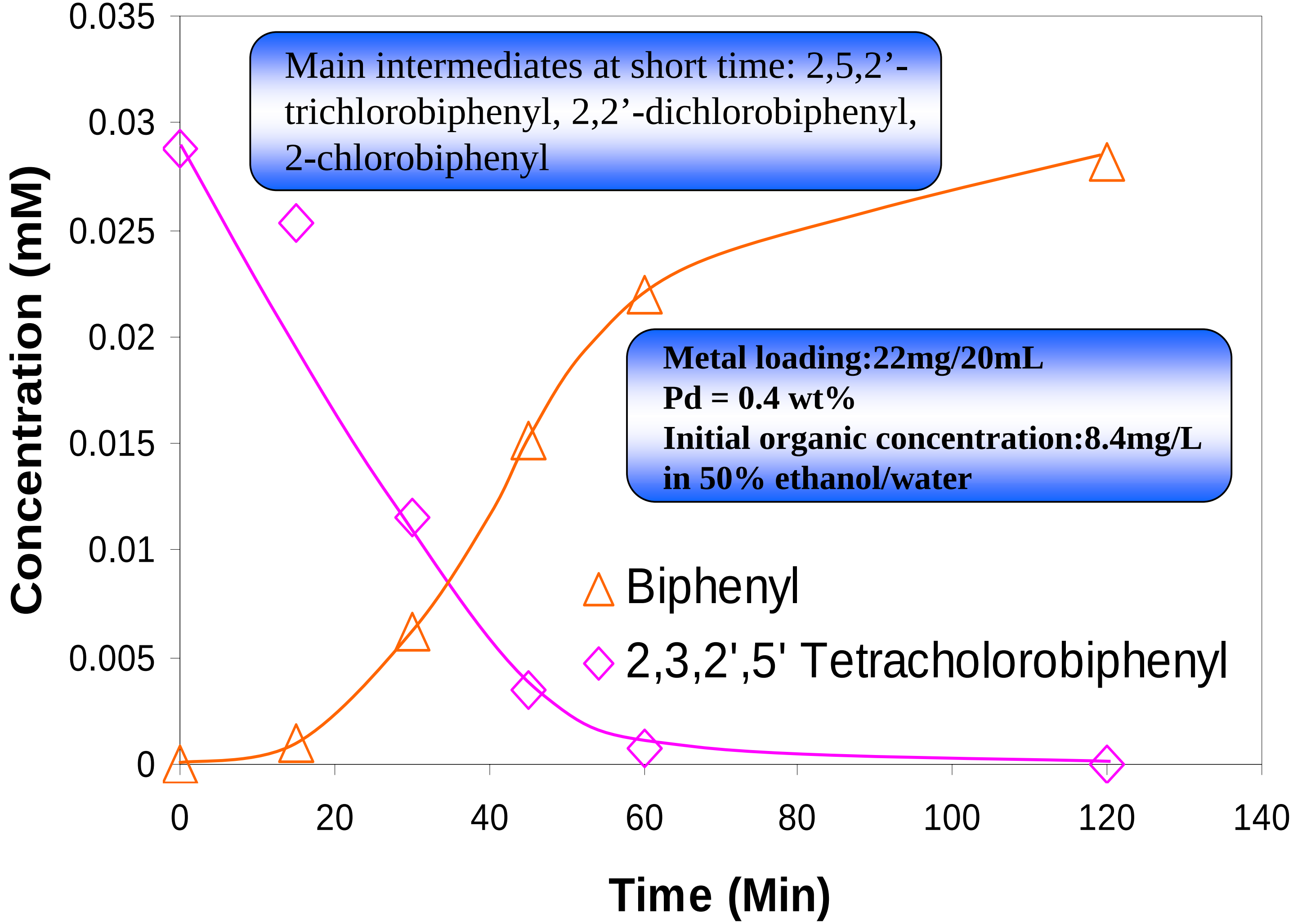
* From B. Schrick, J.L. Blough, A.D. Jones, T.E. Mallouk, Hydrodechlorination of Trichloroethylene to Hydrocarbons Using Bimetallic Nickel-Iron Nanoparticles. Chem.Mater. 2002, 14, 5140-5147.

Effect of Ni content in Fe/Ni particles on K_{SA}

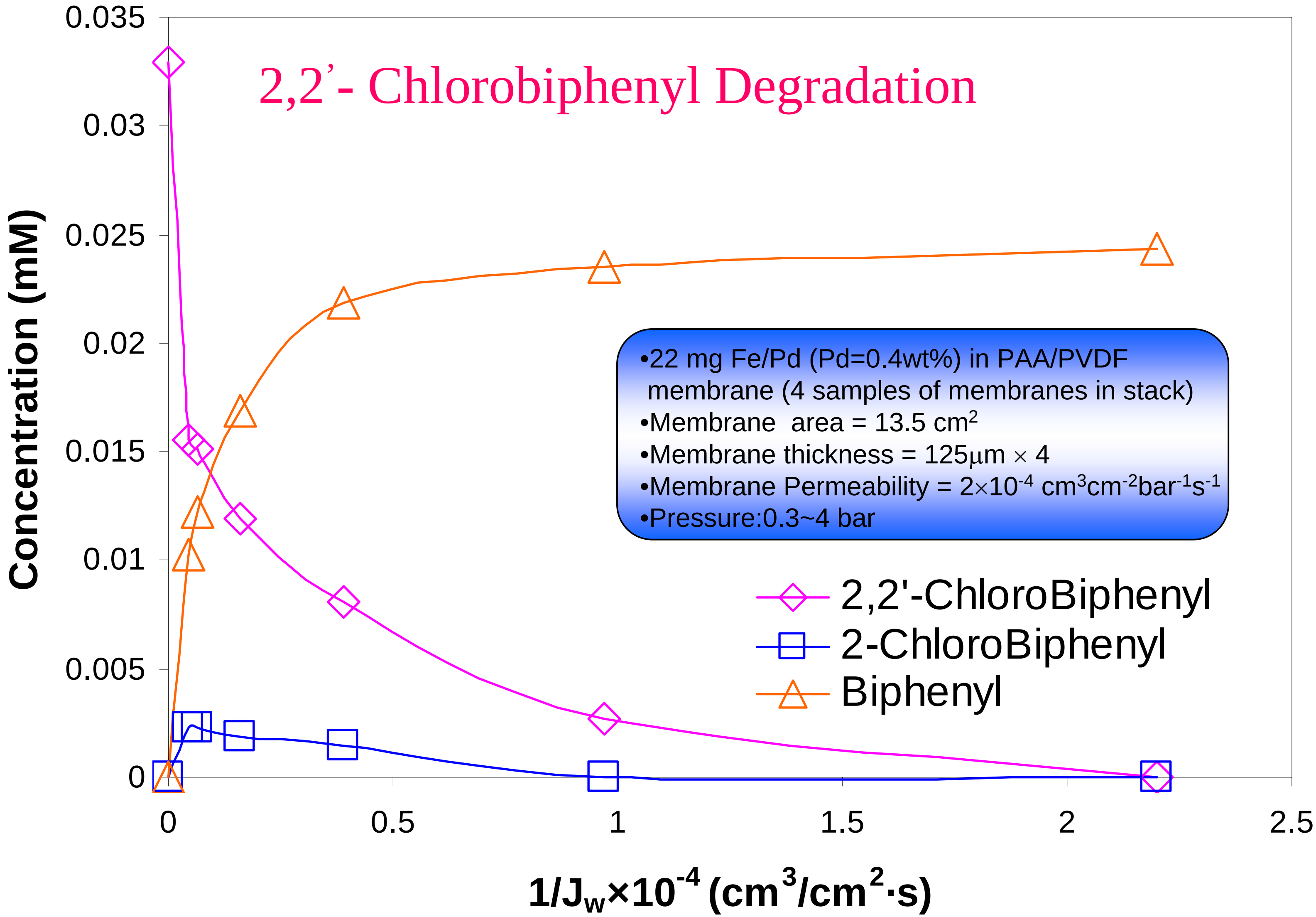


All experiments were performed in batch systems using nanosized Fe/Ni particles (Post coating Ni) immobilized in PAA/PVDF membrane.

Reactions of 2,3,2',5'-Tetrachlorobiphenyl (PCB) with Fe/Pd (~30 nm) in PAA/PVDF membrane



Dechlorination Study under Convective Flow Mode(PVDF-MF membrane & Fe/Pd nanoparticles)



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