NITROGEN AND PHOSPHOROUS REMOVAL BY RED-CALY BALL COATED WITH nZVI

Development of Low-carbon wastewater reuse system using a modified constructed-wetland technology

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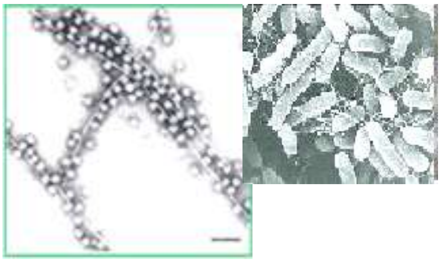
Water Quality Challenges: Emerging Water Contaminants

Pharmaceuticals

Hormones & endocrine disrupting compounds

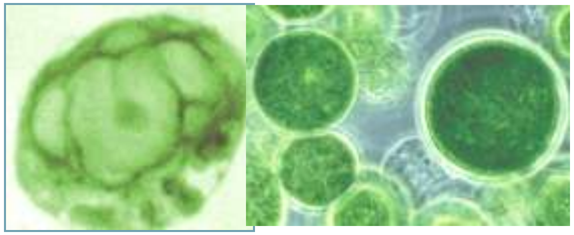
New pathogens



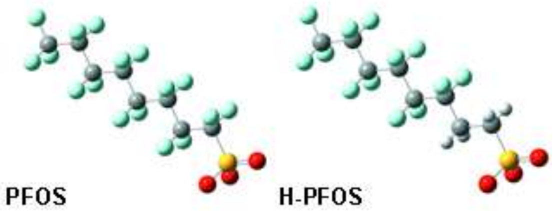
New pesticides & their degradation products

New DBPs (NDMA)

Algal toxins



Perfluorinated compounds



NANOMATERIALS FOR WATER TREATMENT

- **Advantages**

  High surface area ⇒ High reactivity
  Small size ⇒ high mobility and accessibility

- **Examples** **Applications**

TiO_2 nanoparticles
ZnO nanoparticles ⇒ Photo-catalyst

Carbon-based nanomaterials (Fullerene, CNT…) ⇒ Photo-catalyst
Adsorbent
Antimicrobial agent
Membrane material

Iron oxide nanomaterials ⇒ Photo-catalyst
Fenton catalyst

Nanoparticulate zero-valent iron (nZVI) ⇒ Reductant
Fenton catalyst

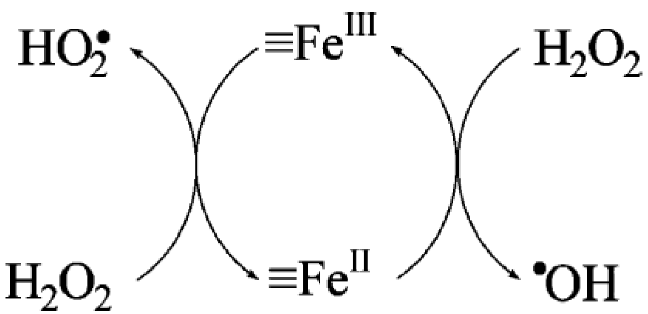
Nanoparticulate bimetals (Fe/Ni, Fe/Pd, Zn/Pd…) ⇒ Reductant

Silver nanoparticles ⇒ Antimicrobial agent

Mesoporous alumina-silica materials (zeolites) ⇒ Adsorbent
Supporter

Iron-Based Nanomaterials for Water Treatment

Haber–Weiss Mechanism



Iron oxide nanomaterials

⇒Catalyst for the activation of H_2O_2 and O_3 into $^{\bullet}OH$

Nanoparticulate zero-valent iron (nZVI)

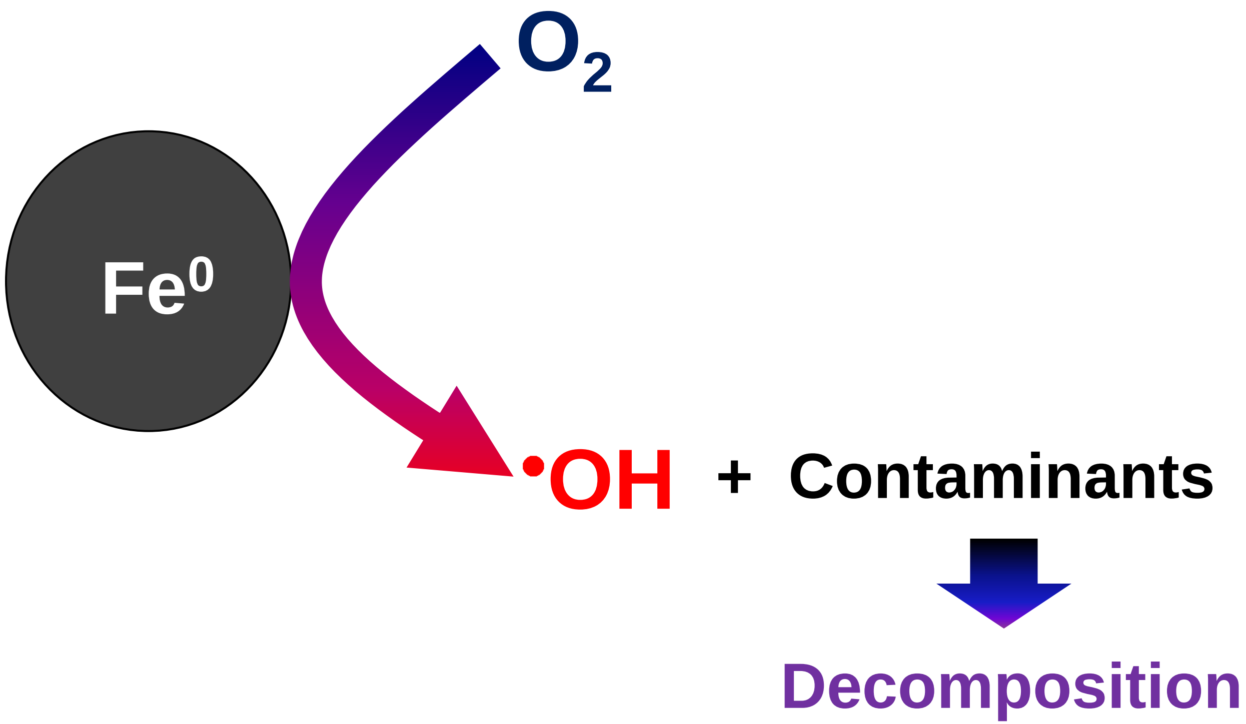
⇒Strong reducer for oxidative contaminats

Iron-based bimetallic nanoparticles

⇒ Reagent for the activation of O_2 into $^{\bullet}OH$
Reducing agent

ZVI for Oxidation of Contaminants

- **Oxidation of 4-Chlorophenol by ZVI**
  (Noradoun et al., 2003, *Ind. Eng. Chem. Res.*)
- **Oxidation of Molinate by nZVI**
  (Joo et al., 2004, *ES&T*)



Iron Oxide Nanomaterials

- **Silica-supported iron oxide working at neutral pH**
  (Pham et al., *ES&T*, 2009)

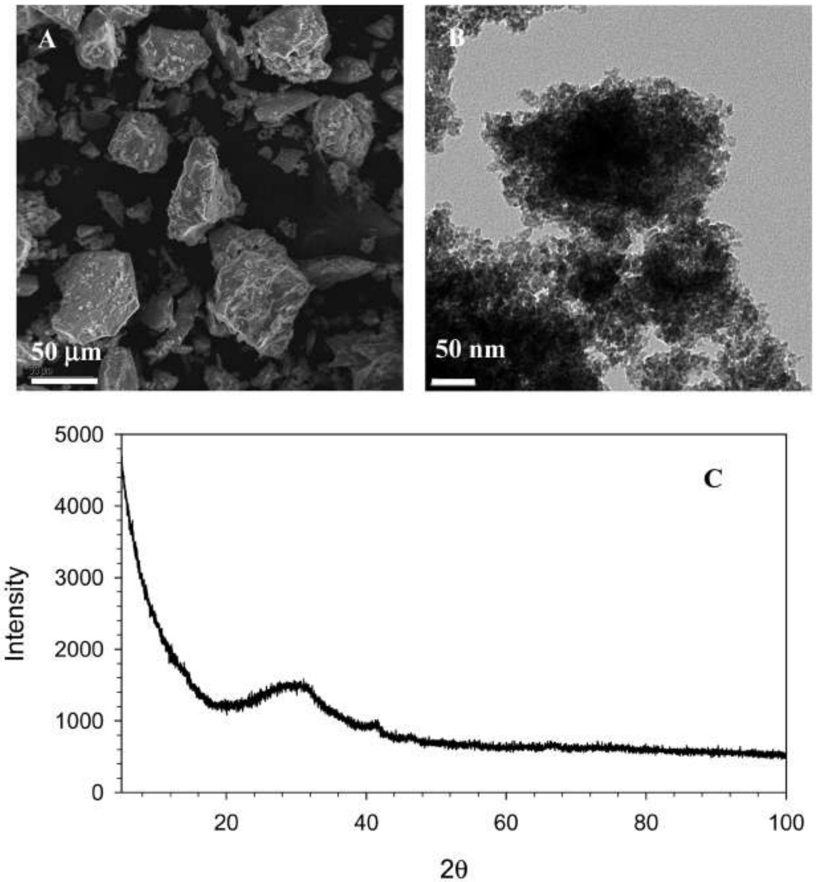


FIGURE 1. FeAlSi-ox obtained by sol−gel processing of an aqueous mixture of $Fe(ClO_4)_3$, $Al(NO_3)_3$, and TEOS: (A) SEM, (B) TEM, and (C) XRD.

type of material	BET surface area (m^2/g)	Fe content (wt %)	Al content (wt %)
hematite	35.9	70[a]	–
goethite	13	35[b]	–
amorphous FeOOH	165.8	62.9[a]	–
FeSi-ox	521	12.3	–
FeAlSi-ox	423	10.9	4.95

[a] Theoretical value. [b] Value reported by the manufacturer.

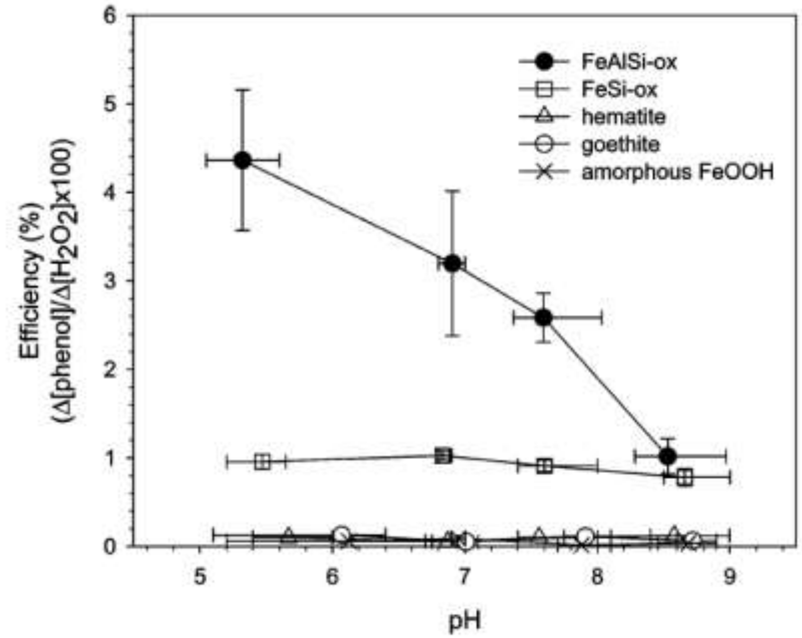


FIGURE 5. Stoichiometric efficiency (Δ[phenol]/Δ[H_2O_2] × 100%) as function of pH. Data collected when Δ[phenol] = 23−27% [phenol]$_o$. [Phenol]$_o$ = 0.5 mM; [H_2O_2]$_o$ = 50 mM; [oxide] = 3 g/L.

Zero-Valent Iron

Zero-Valent Iron (ZVI)

1) Effective material in removing a broad range of organic and inorganic pollutants (heavy metals, Freons, pesticides, nutrients, etc.)

2) Mechanism – Adsorption, Reduction, Oxidation

ZVI for reduction of contaminants (Arnold and Roberts, *ES&T*, 2000; Farrell et al., *ES&T*, 2000)

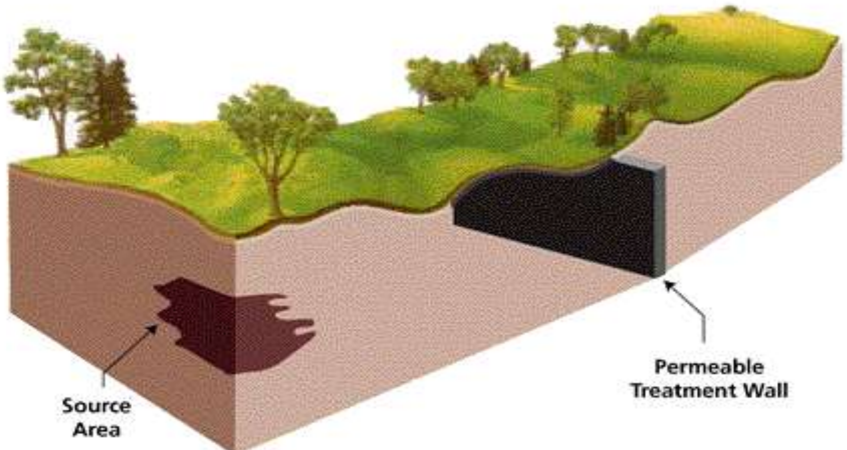
1) $Fe^0 \rightarrow Fe^{2+} + 2e^-$ ($E^0 = -0.447\ V_{NHE}$)

2) Dechlorination:

$$R\text{-}Cl + e^- \rightarrow R^\bullet + Cl^-$$

3) Denitrosation:

$$NDMA + e^- \rightarrow DMA + {}^\bullet NO$$

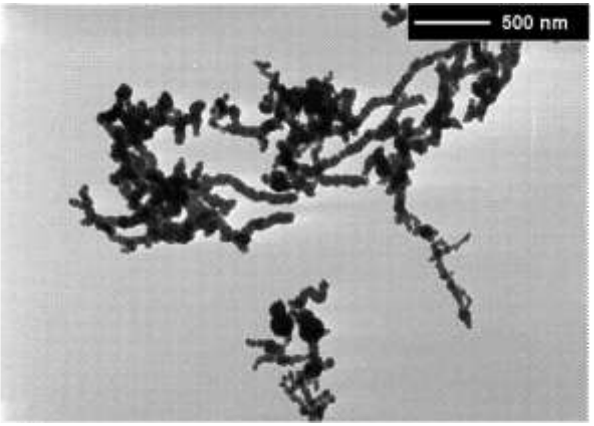


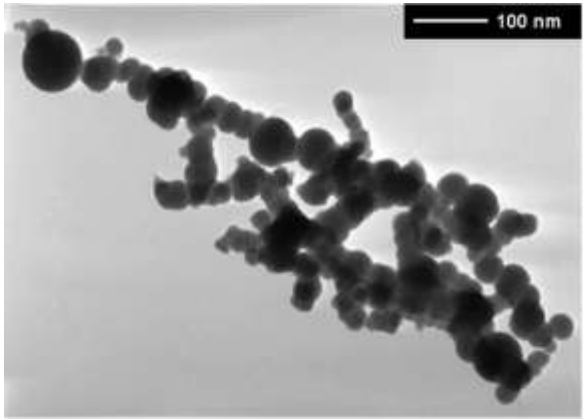
<nZVI as permeable reactive barrier>
(http://www.epa.gov)

Nanoparticulate Zero-Valent Iron(nZVI)

- **Granular Zero-Valent Iron**

- **Nanoparticulate Zero-Valent Iron (nZVI)**



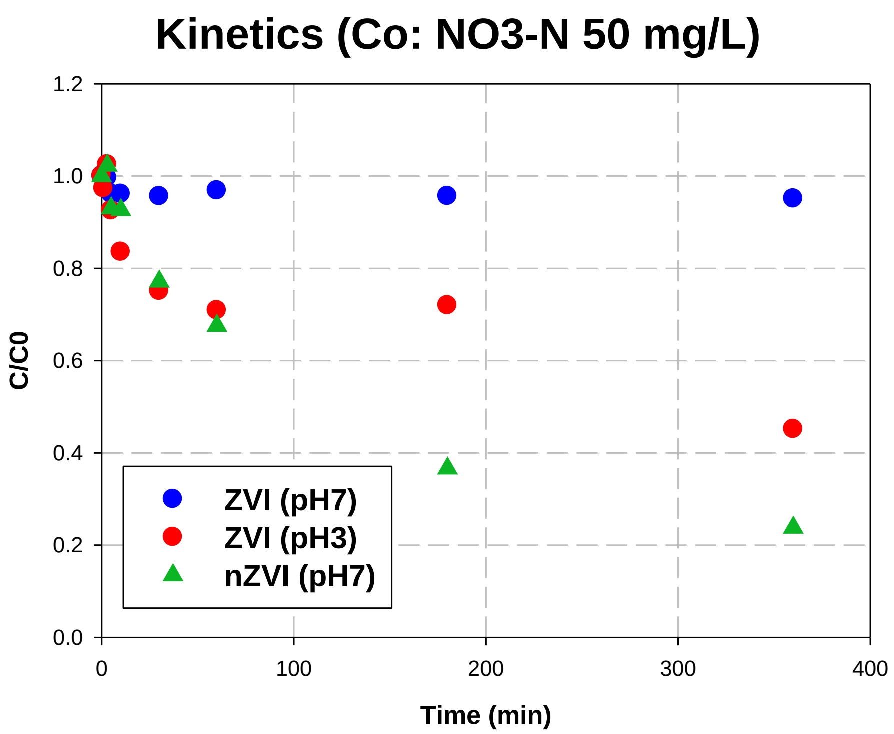


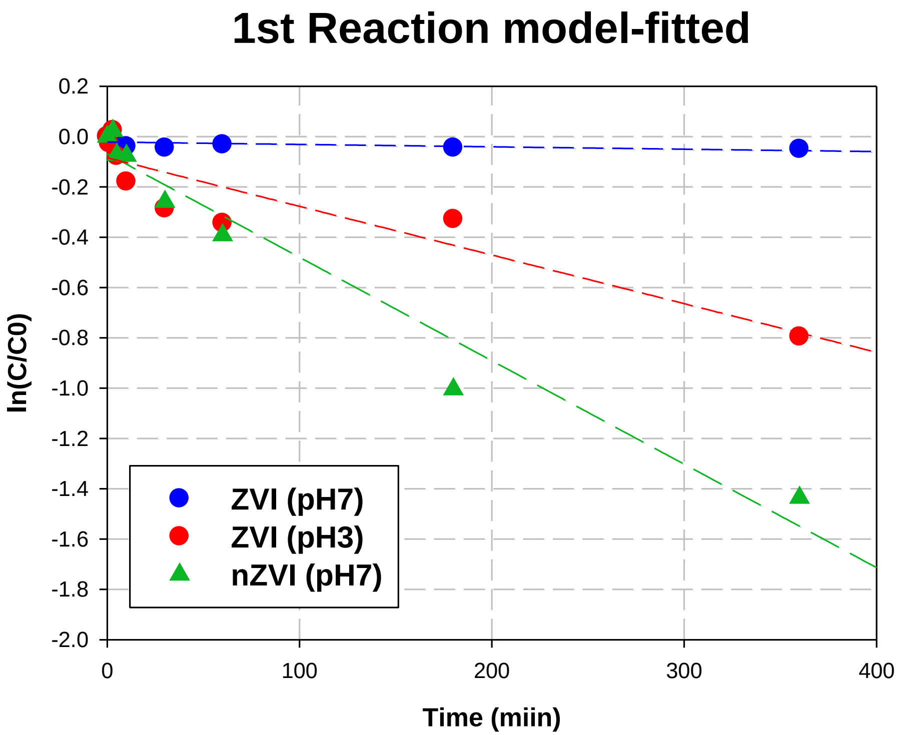
Particle size:
1 ~ 100 nm
(av. ~ 50 nm)

Surface area:
31.5 m^2/g

⇑ **TEM images of nZVI synthesized by liquid-phase reduction**

ZVI REACTIVITY TEST (SIZE, PH VARIATION)





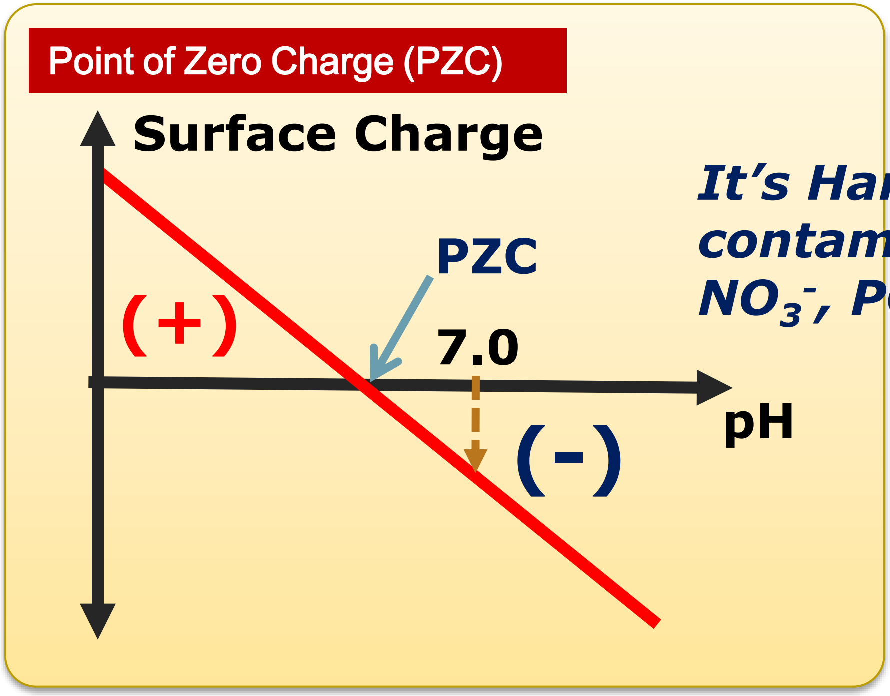
*1st Reaction model

$$\frac{d[A]}{dt} = -k \cdot [A]$$

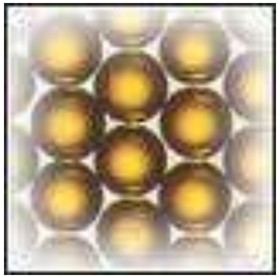
	ZVI (pH 7)	ZVI (pH 3)	nZVI
k [1/min]	**9.0×10^{-5}**	**1.9×10^{-3}**	**4.0×10^{-3}**
R^2	**0.8**	**0.84**	**0.96**

NEW ADSORBENT FOR ANION ADSORPTION

*** Adsorbent of anions**



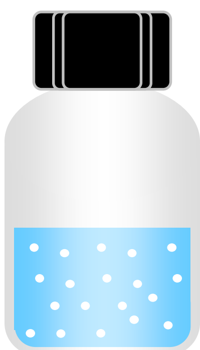
It's Hard to adsorbe the anion contaminants such as NO_3^-, PO_4^{3-}, CrO_7^-, $As_2O_3^-$!!



Expensive !
Anion exchange resin
(16 €/kg)

NEW ADSORBENT FOR ANION ADSORPTION

- **SMZ (Surface modified zeolite) (Li, Z and Bowman, R.S.,1997)**
  - modifying the surface of natural zeolite with surfactant bilayer



Shaking raw zeolites with HDTMA-Br solution 24 hr

SMZ with Surfactant bi-layer coated

Dry in the air after washing D.I .water

Decant the supernatant after centrifuge

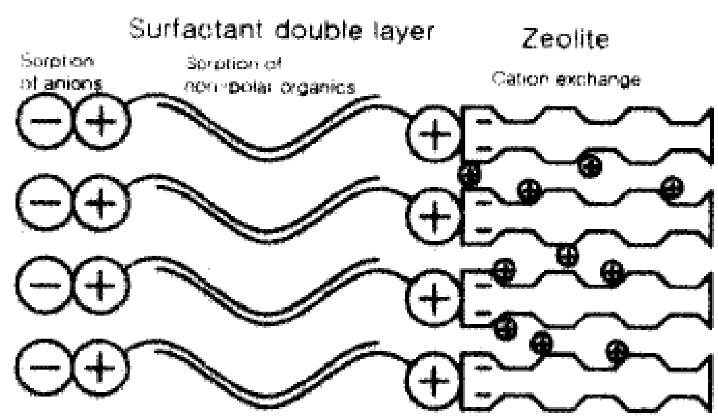


Fig. 2 Cationic Surfactants forming a bilayer on the Zeolite surface

NEW ADSORBENT FOR ANION ADSORPTION

- **Fe-loaded zeolite (Lee, 2003)**
  - Using zeolite as a support material, adsorb ferrous(ferric) ion on to the surface and inner pore of the zeolite. And then reducing the iron ions into zero valent by adding of strong reducing agent($NaBH_4$).

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$$

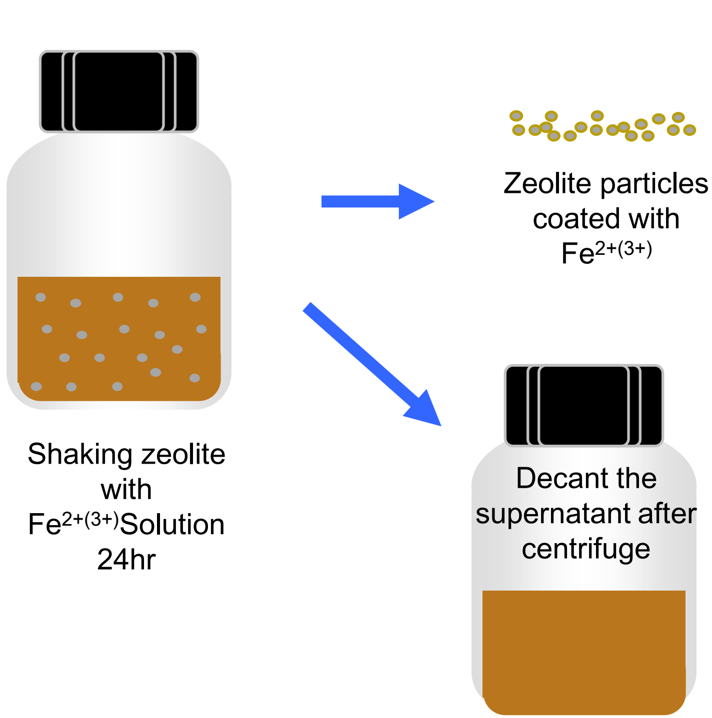
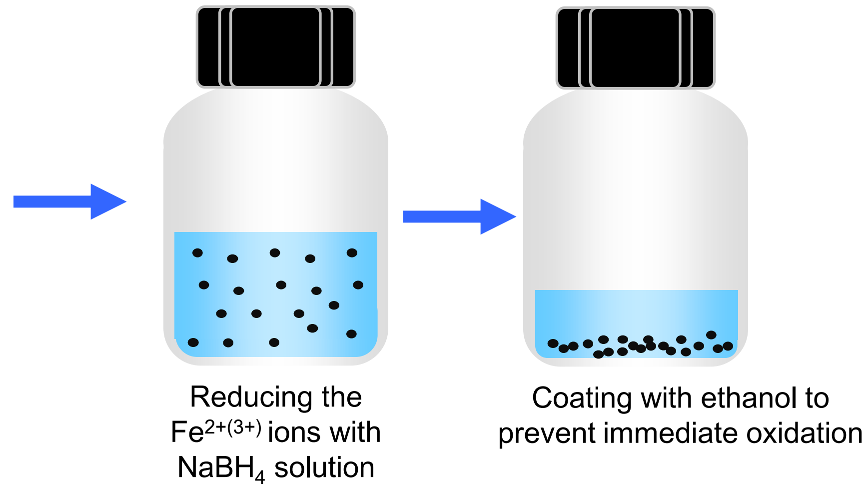



Fig.| Fe-loaded zeolite made from $FeSO_4$(left), raw zeolite(center), one made from $FeCl_3$(right)

NEW ADSORBENT FOR ANION ADSORPTION

- **Red-clay ball coated with nZVI (Chung, 2010, Korean patent No. 100978589)**

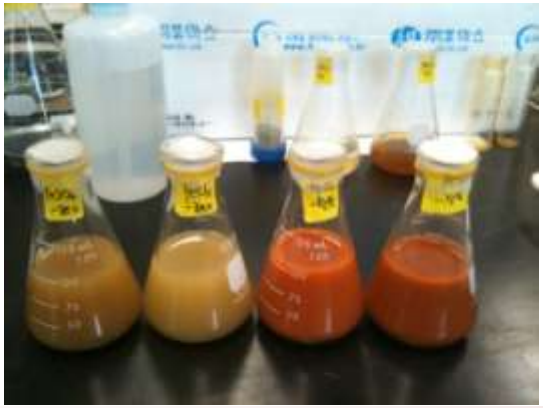
- Red-clay is specific soil from Gochang, Korea , which is abundant of minerals such as Al, Mg, Fe and these cations make insoluble precipitations with phosphate.

Make spherical shape adding small amount of D.I water and Calcination With 900’C furnace

$Fe^{2(3)+}$ Solution

Shaking with $\mathbf{FeCl_3}$, $\mathbf{FeSO_4}$ solution and reducing with $NaBH_4$

nZVI-coated red-clay ball

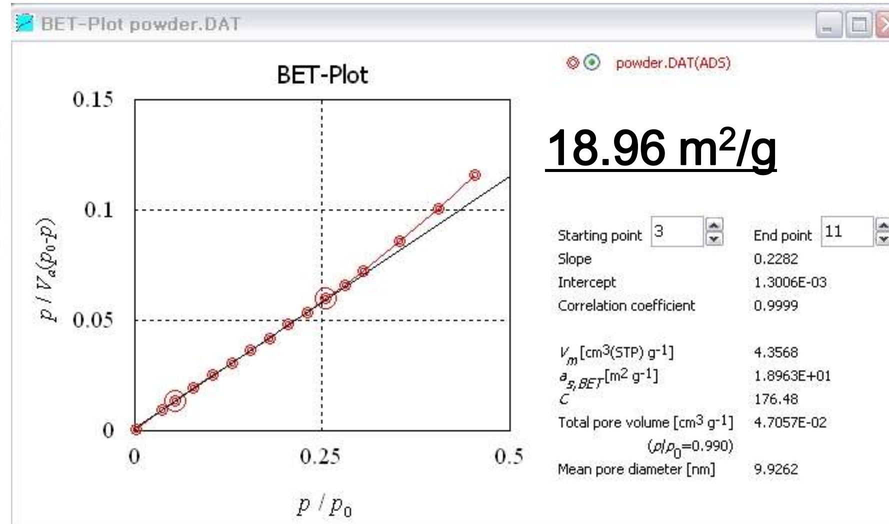


Shaking with $Fe^{2(3)+}$ Solution

CHRACTERISTICS of RED-CLAY

Red-Clay from Go-chang, Korea

* Surface Area (BET analysis)

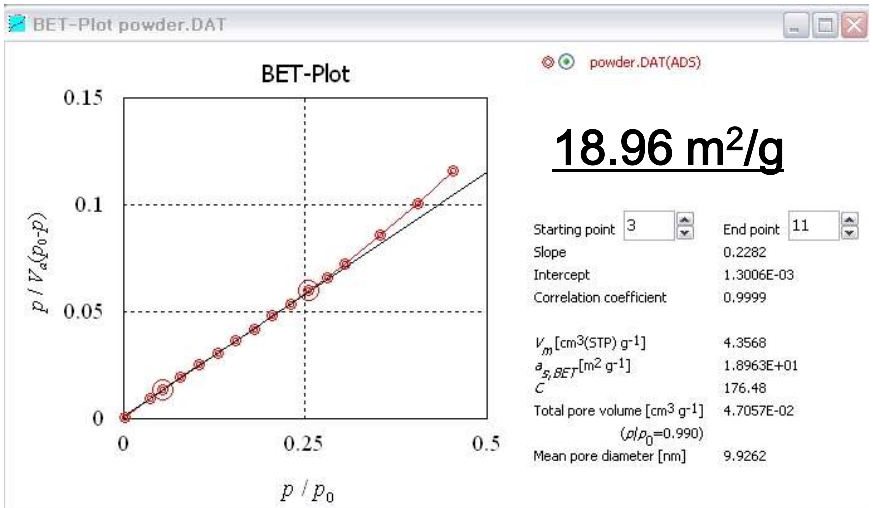


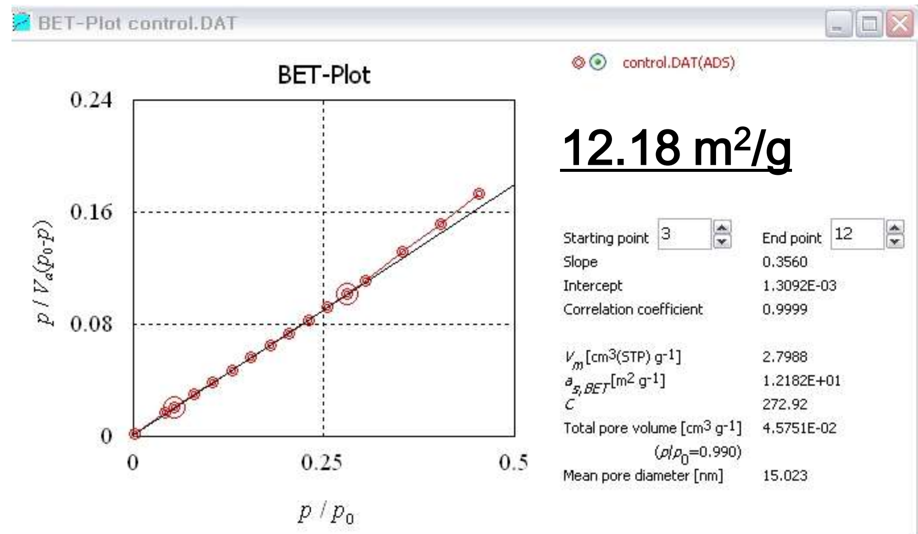
* Compositions (XRF analysis)

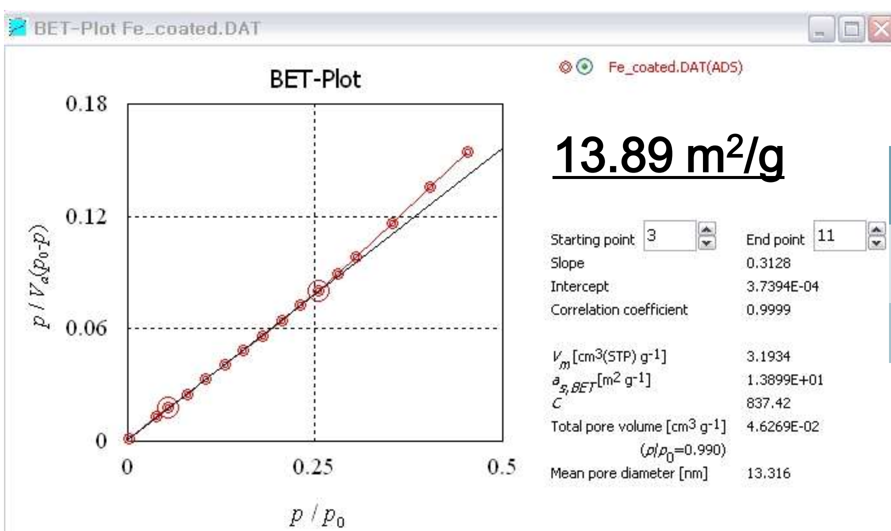
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K2O	MnO	P_2O_3	LOI	Total
zeolite	66.2	13.2	0.3	1.53	0.1	3.09	2.56	1.57	0.1	0.12	10.92	100.25
Bottom ash	4.45	0.36	0.05	92.46	0.01	0.05	0.03	0	1.01	0.09	1.94	100.45
Red-Clay	**60**	**17**	**1.6**	**19**	**-**	**0.32**	**-**	**1.8**	**0.19**	**0.06**	**-**	**99**
residual soil	67.65	18.27	0.1	1.44	0.26	0.27	4.26	4.85	0.1	0.02	2.29	99.5

CHRACTERISTICS of RED-CLAY

- **Comparison of Surface Area between powdered, after Calcination and nZVI on it**





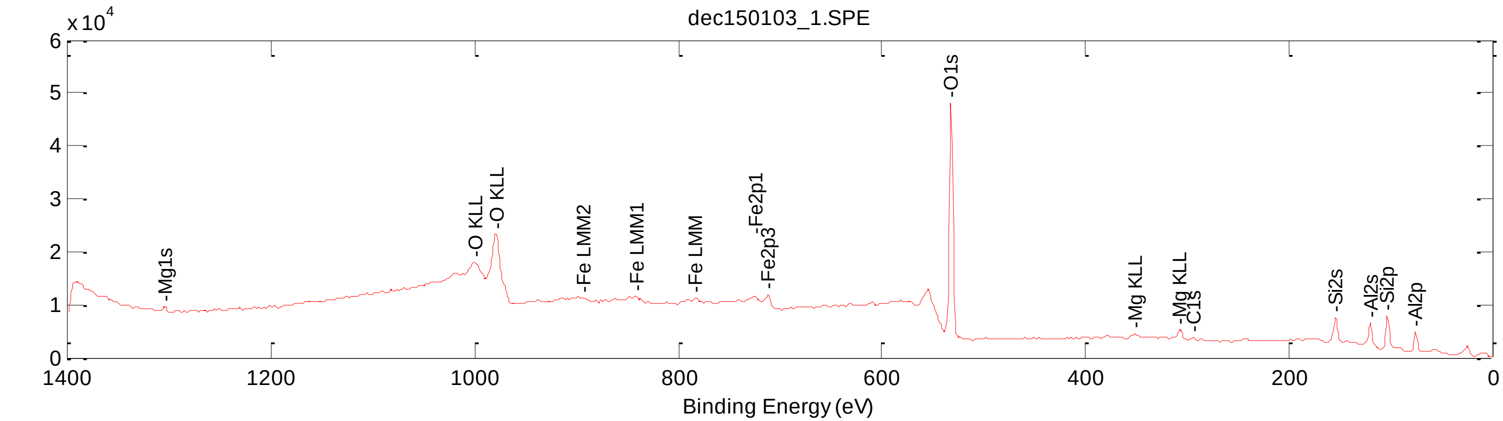


	Powdered	After Calcination	nZVI-coated
$a_{S,BET}$ [m^2/g]	**1.89 x10^1**	**1.22 x10^1**	**1.39 x10^1**
R^2	**0.99**	**0.99**	**0.99**

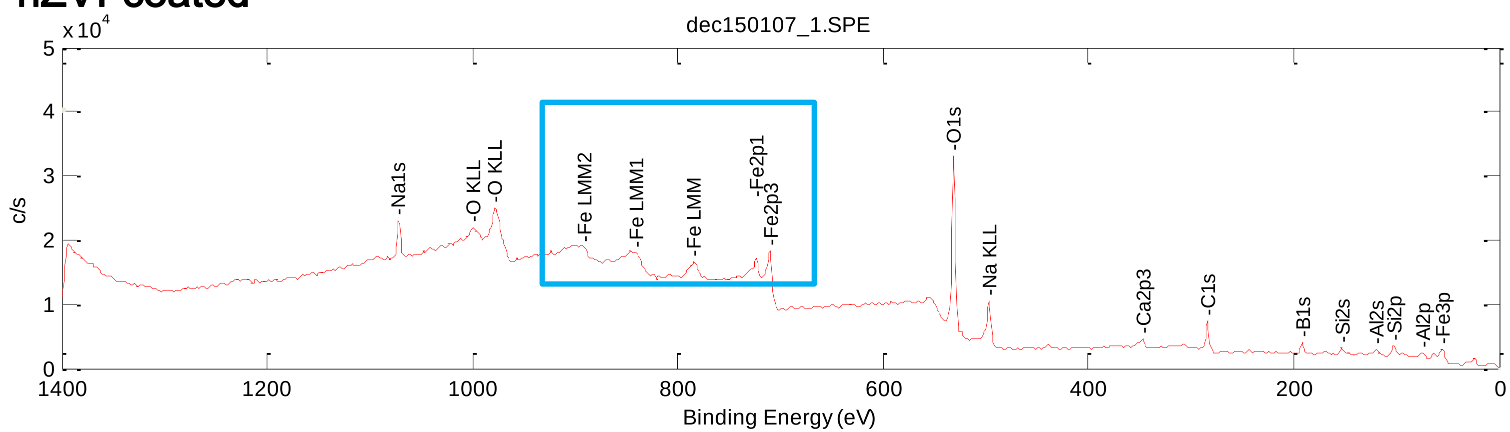
CHRACTERISTICS of RED-CLAY

* Verification of coated Fe (XRD results)

Controll



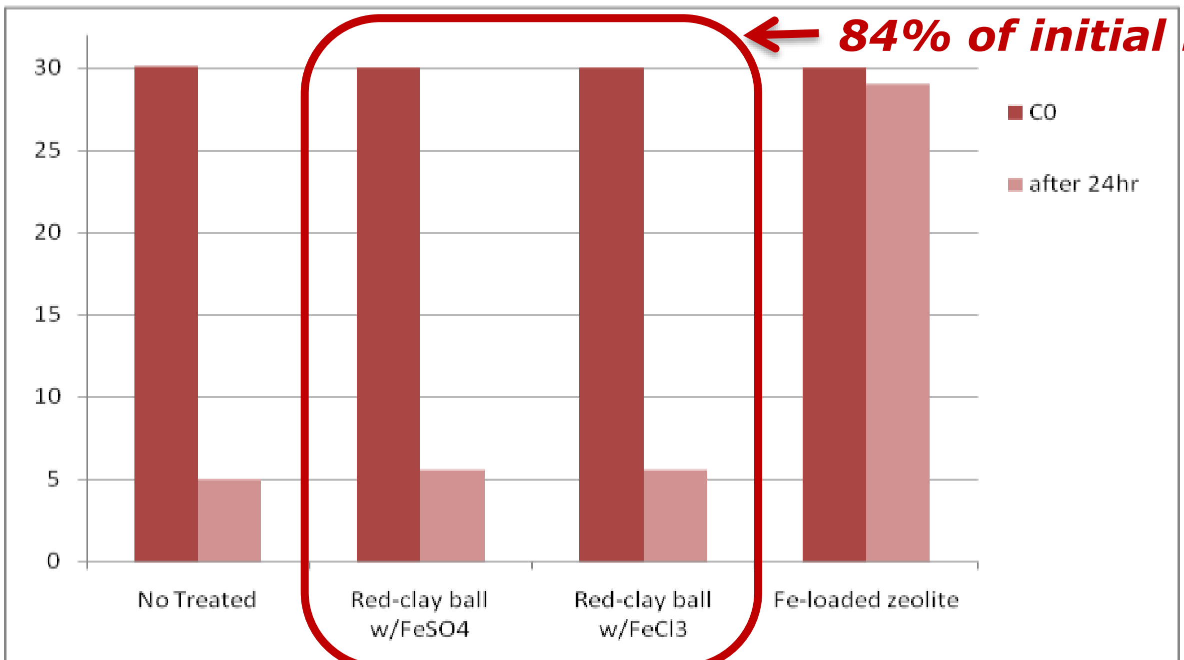
nZVI-coated



PO_4^{3-} REMOVAL EFFICIENCY USING VARIOUS ADSORBENT

Batch Procedure

Weighing	Agitation	Filtering	Measuring
			



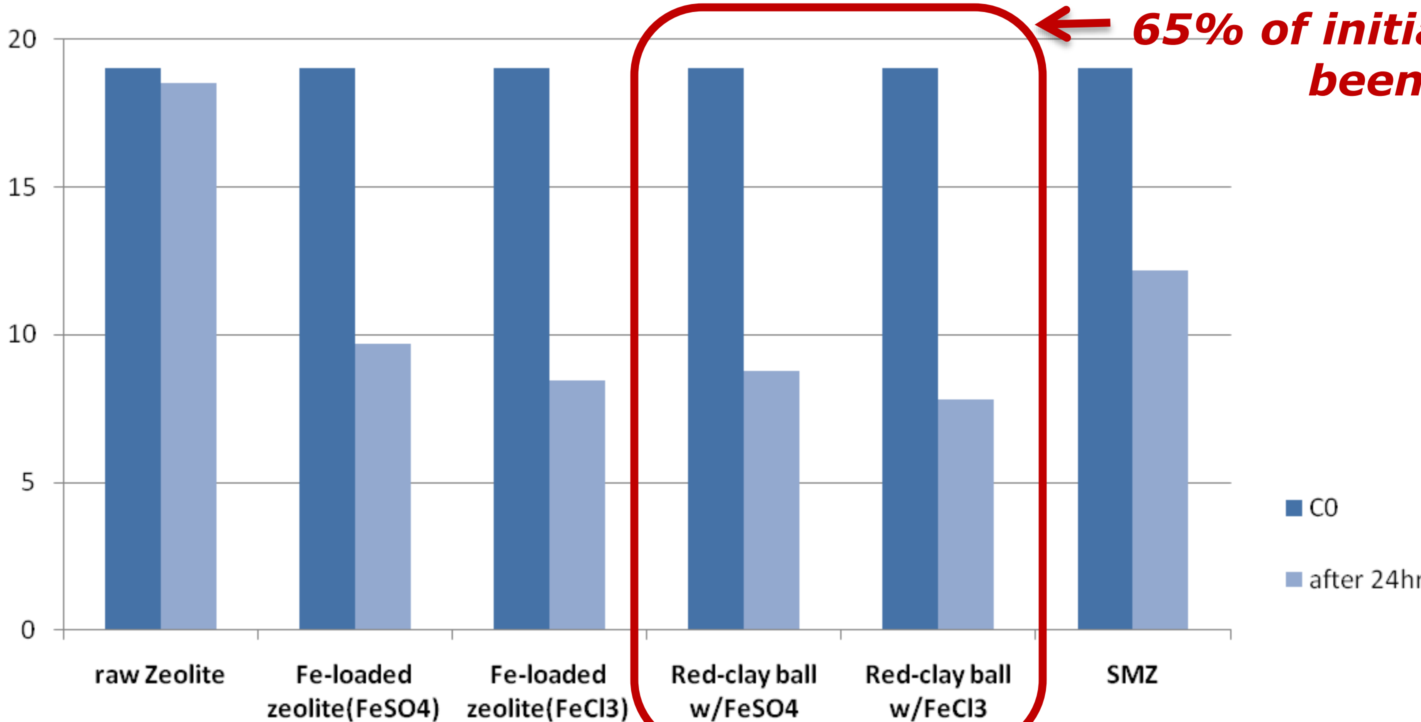
84% of initial PO4 has been removed!

(Unit: mg/L)

NO_3^- REMOVAL EFFICIENCY USING VARIOUS ADSORBENT

Batch Procedure

Weighing | Agitation | Filtering | Measuring



65% of initial NO_3 has been removed!

(Unit: mg/L)

RESIDUAL NH_3 & BREAKTHROUGH

- **Different by-product between using ZVI & nZVI**

ZVI Pathway: $\mathbf{NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + \underline{NH_4}^+ + 3H_2O}$

nZVI Pathway: $\mathbf{2NO_3^- + 5Fe^0 + 6H_2O \rightarrow 5Fe^{2+} + \underline{N_2} + 12OH^-}$

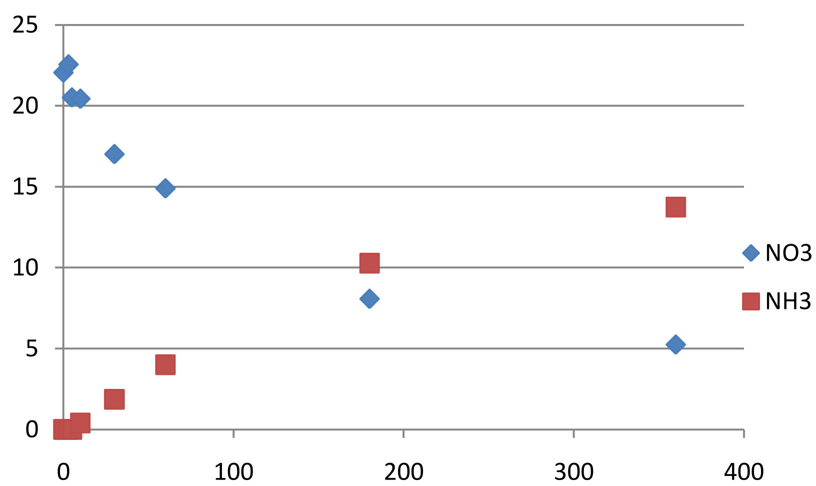


Fig.| NH_3 production during ZVI-NO3 reaction

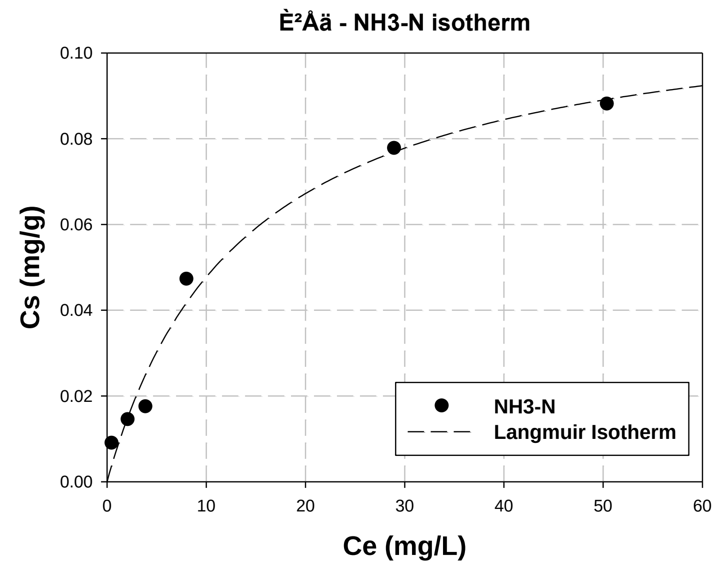


Fig.| NH_3 Langmuir Isotherm Curve for Red-Clay ball

CONCLUSION

- Various nano-materials were synthesized in lab condition and their reactivity was tested for nitrogen and phosphorous.

- nZVI is not only a good reducer but also effective catalyst for producing oH· radicals.

- Nitrate, representative anion contaminant, can be effectively removed with nZVI in nutral pH.

- nZVI coated Red-clay ball can simultaneously remove nitrate and phosphate without producing secondary contaminant, ammonia.

“GRACIAS !”

THANK YOU

“감사합니다 !”