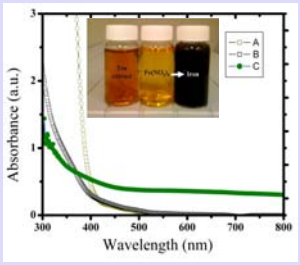
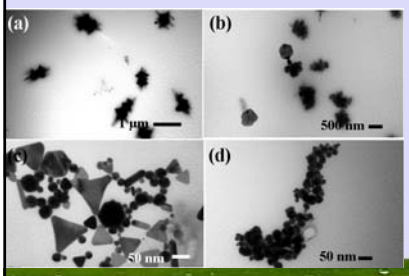
Green Synthesis of Fe^0 and Bimetallic Fe^0 for Oxidative Catalysis and Reduction Applications





presented by

George E. Hoag[1], Ph.D.
Senior Vice-President

John B. Collins[1], PhD., Jessica R. Hoag[1] and Jennifer L. Holcomb[1], Rajender Varma[2], Ph.D., Mallikarjuna N. Nadagouda[2], Ph.D.

[1]VeruTEK Technologies, Inc.
65 West Dudley Town Road, Bloomfield, CT 06002 USA
www.verutek.com

[2]National Risk Management Research Laboratory (NRMRL)
U.S. Environmental Protection Agency
Cincinnati, OH, USA

VeruTEK TECHNOLOGIES

Acknowledgements

- John Collins, Ph.D. President/CEO VeruTEK®
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- Mallikarjuna N. Nadagouda, Ph.D., Chemist
  U.S. Environmental Protection Agency
  National Risk Management Research Laboratory (NRMRL)
- Jennifer L. Holcomb – Chemist, VeruTEK®
- Jessica R. Hoag – Chemist, VeruTEK®

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VeruTEK TECHNOLOGIES

References

Journal Articles

1) George E. Hoag, John B. Collins, Jennifer L. Holcomb and Jessica R. Hoag, Mallikarjuna N. Nadagouda and Rajender S. Varma. Degradation of bromothymol blue using nano iron synthesized through greener method. ***RSC J. Mater. Chem.,*** 2009, DOI: 10.1039/b909148c
2) Mallikarjuna N. Nadagouda, George Hoag, John Collins and Rajender S. Varma. Green synthesis of Au nanostructures at room temperature using biodegradable plant surfactants, **ACS Journal of Crystal Growth and Design**. 2009, (In Press, available online in Oct. 2009)
3) Babita Baruwati, Rajender S Varma, High Value Products from Waste: Grape Pomace Extract - A Three-in-One Package for the Synthesis of Metal Nanoparticles, **ChemSUSChem**, 2009 (In Press, available online in Oct. 2009)

Related Information

USEPA- VeruTEK® - Cooperative Research and Development Agreement (CRADA)

Patent Pending – VeruTEK®/USEPA

VeruTEK TECHNOLOGIES

Fe^0 Nanometal Synthesis

- **Two Common Existing Manufacturing Methods**

- **Liquid Method – Sodium Borohydride Reduction**

- **Attrition Method – Mechanical Grinding**

- **Many Other Methods**
  - **– Mostly for non environmental applications**

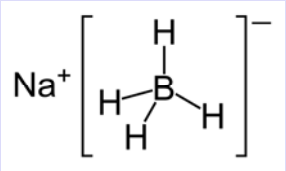
- **Capping Agents**

VeruTEK TECHNOLOGIES

Fe^0 Nanometal Synthesis

Sodium Borohydride Reduction

Excess Required



$$+ \quad FeCl_3 \longrightarrow Fe^0 + H_{2(gas)} + \text{products}$$

- $NaBH_4$ is highly toxic, corrosive and flammable – highly hazardous material
- Borohydride reaction is aggressive with gas production
- Excess borohydride needed and present in products
- Must be rinsed from nZVI and is a listed hazardous waste
- Rinsed Fe_0 is not capped and is subject to corrosion, if dried can be reactive with oxygen gas

VeruTEK TECHNOLOGIES

Fe^0 Nanometal Synthesis

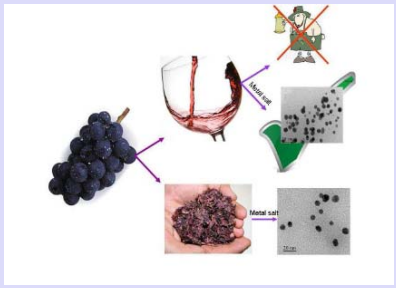
Mechanical Attrition - Grinding

- Costly, energy intensive and waste producing
- Not capped and subject to corrosion and combustion with oxygen if dry

VeruTEK TECHNOLOGIES

Green Synthesis Nanometals

- Uses only plant extract polyphenols and sources of dissolved metals
- Polyphenols come from many plant materials and plant processing waste streams
- Many fruits, vegetables, herbs and grains contain high concentrations of polyphenols
- Tea, grapes, sorghum bran (up to 5% polyphenols)
- Polyphenols can be either warm water (80^{0}C) or cold water and ambient pressure, surface reactions
- Can concentrate polyphenols if desired but not necessary
- Extensive research exists on polyphenol antioxidant properties of plants



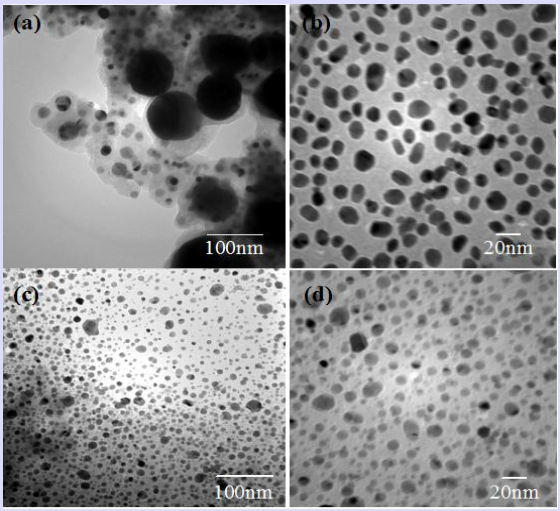
VeruTEK TECHNOLOGIES

Types of Nanometals Manufactured with This Process

- Fe, Ag, Au, Pd, Pt, bimetallic
- Polyphenols are reducing agent and the capping agent – antimicrobial and antifungal
- The polyphenolic biopolymer capping agent greatly affects the reactivity of the nanometals
- G-nZVI Fe^0 is not subject to oxidation during storage because polyphenols are antioxidant
- Polyphenols scavange free radicals
- In most cases do not need or want to wash off polyphenol

VeruTEK TECHNOLOGIES

TEM images of Ag and Pd Nanoparticles in Aqueous Solution of Coffee and Tea Extract



Notes: Casted on Cu grid coated with carbon, (a-b) Ag nanoparticles from coffee and tea extract, respectively, and (c-d) Pd nanoparticles from coffee and tea extract, respectively.

VeruTEK TECHNOLOGIES

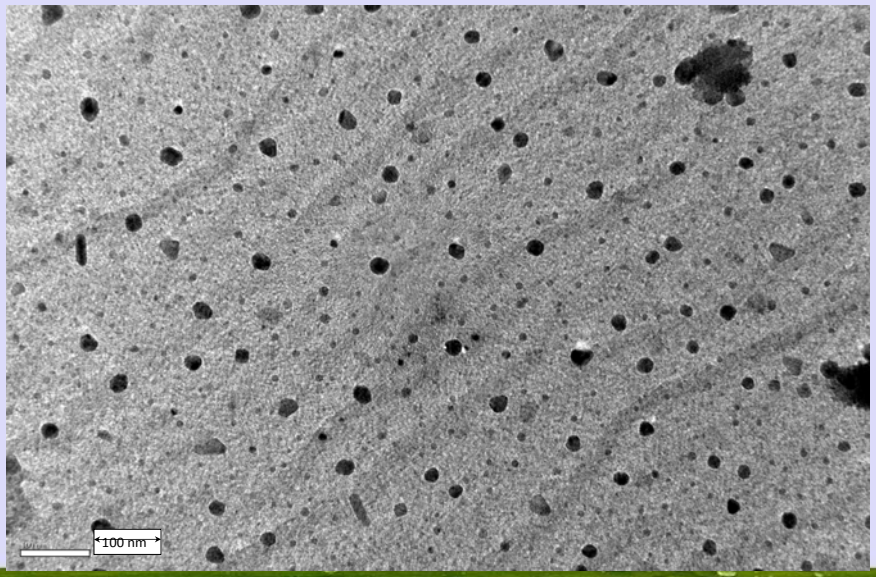
Formation of Nanoscale Zero Valent Iron Particles by Mixing Green Tea Extract with Ferric Chloride

VeruTEK TECHNOLOGIES

Formation of Nanoscale Zero Valent Iron Particles by Mixing Green Tea Extract with Ferrous Sulfate

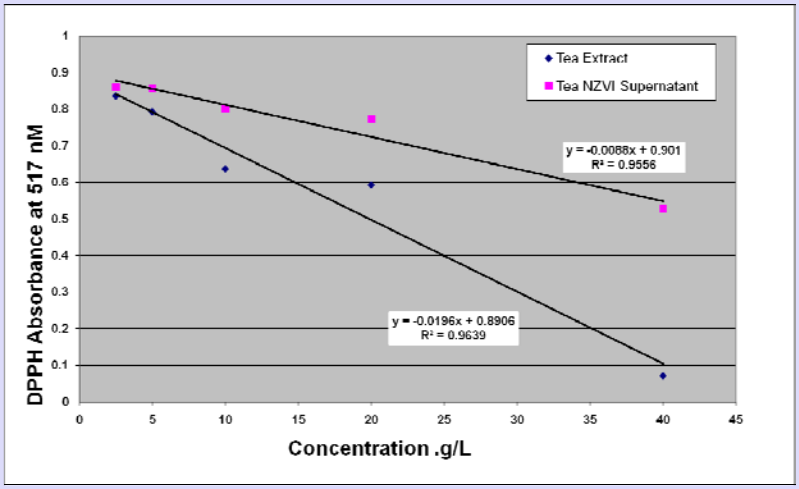
VeruTEK TECHNOLOGIES

Green Tea Synthesized Zero Valent Iron Nanoparticles 0.1 M Ferric Chloride



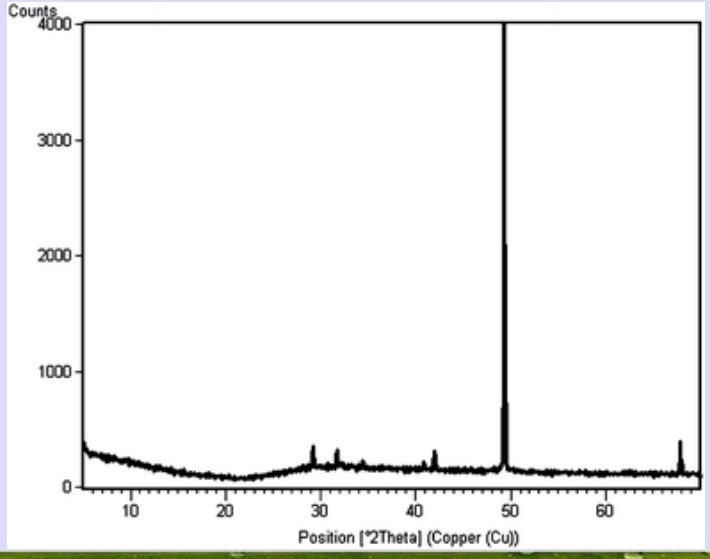
VeruTEK TECHNOLOGIES

Plant Extract DPPH Stable Radical Consumption Nanoscale Zero Valent Iron Particle Formation from Reaction of Green Tea Extract with Ferric Chloride



VeruTEK TECHNOLOGIES

Representative XRD Pattern of Iron Nanoparticles Synthesized Using Tea Extract



VeruTEK TECHNOLOGIES

Chlorinated Solvent DNAPL Dyed with Suidan IV and Complete Dissolution in VeruSOL-3™

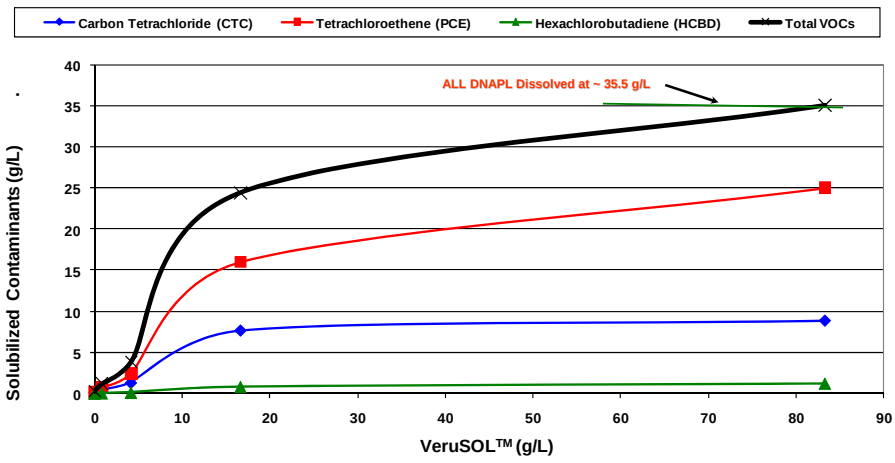
VeruSOL™

- Mixture of Plant Oil Based Surfactants +/- Citrus Terpenes
- Biodegradable Oils
- Forms Emulsions – Colloids
- Enables Aqueous Reactions to Treat NAPL Phase

VeruTEK TECHNOLOGIES

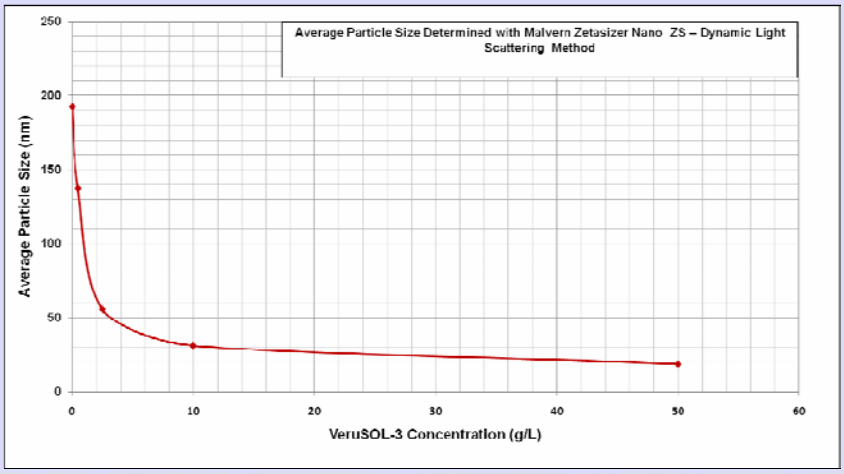
Chlorinated Hydrocarbon Dissolution Example

Effect of VeruSOL™ on DNAPL Solubilization
(Concentration VeruSOL™ vs. Solubilized VOCs)



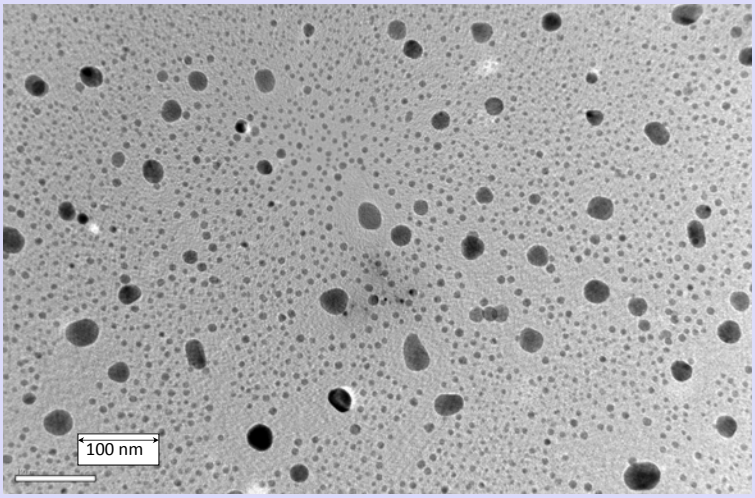
VeruTEK TECHNOLOGIES

Micelle Particle Size Chlorinated Solvent DNAPL – VeruSOL-3™

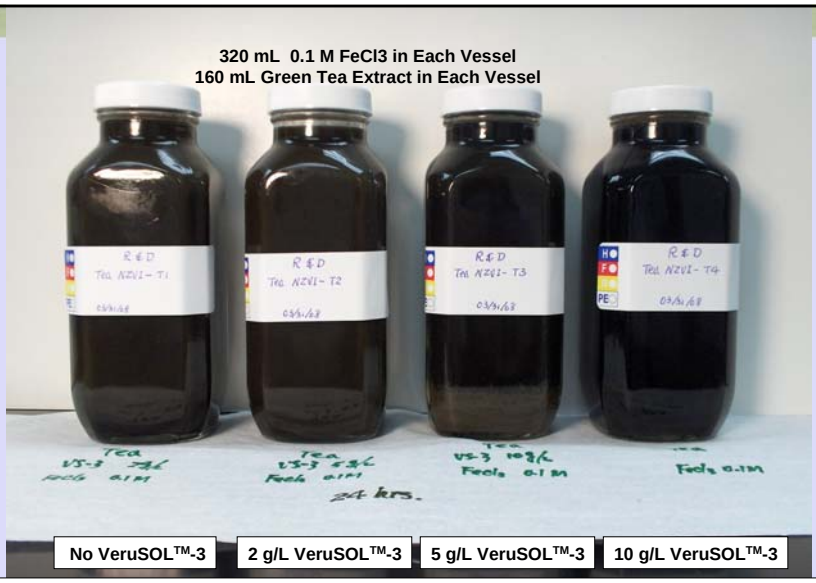


VeruTEK TECHNOLOGIES

Green Tea Synthesized Zero Valent Iron Nanoparticles 0.1 M Fe(III)-EDTA with 5 g/L VeruSOL™-3



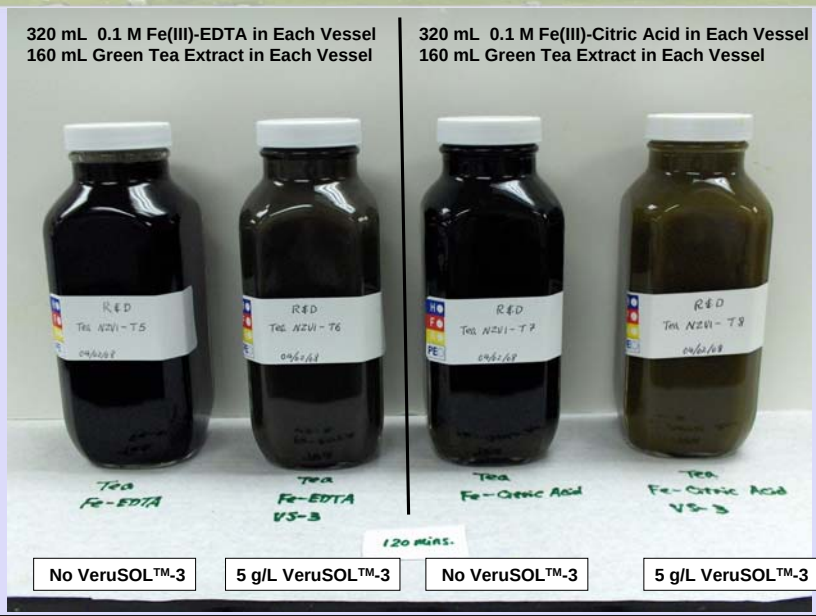
VeruTEK TECHNOLOGIES



Production of nZVI with Green Tea and Ferric Chloride in the Presence and Absence of VeruSOL™-3

Note: Photograph Taken after 24 hours

VeruTEK TECHNOLOGIES

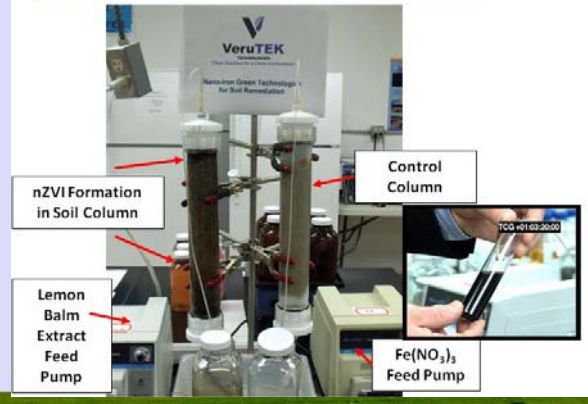


Production of nZVI with Green Tea and Chelated Iron in the Presence and Absence of VeruSOL™-3

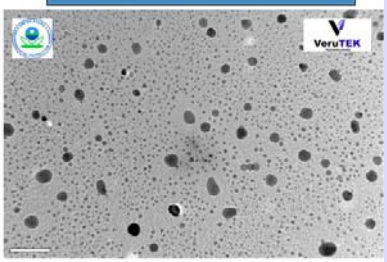
Note: Photograph Taken after 120 minutes

In Situ Green Synthesis of Nano Zero Valent Iron With Plant Extracts

***In Situ* Formation of Nanoparticle Zero Valent Iron in Soils with Lemon Balm Extract with $Fe(NO_3)_3$**



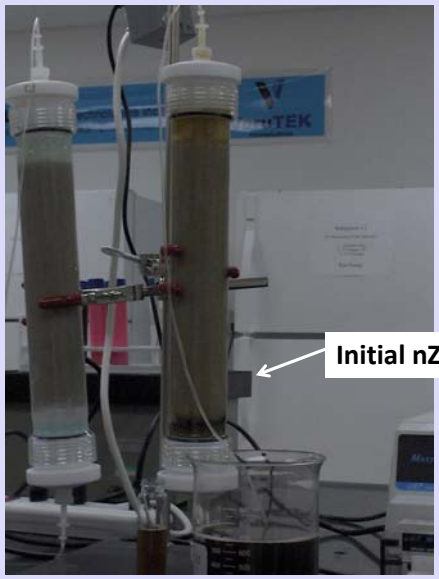
Green Tea Synthesized Zero Valent Iron Nanoparticles with 0.1 M Fe(III)-EDTA with 5 g/L VeruSOL™-3



Transmission Electron Micrograph
Scale Bar = 100 nm

VeruTEK TECHNOLOGIES

Initial Formation of Nanoscale Zero Valent Iron in Soil Column Lemon Balm Extract with $Fe(NO_3)_3$

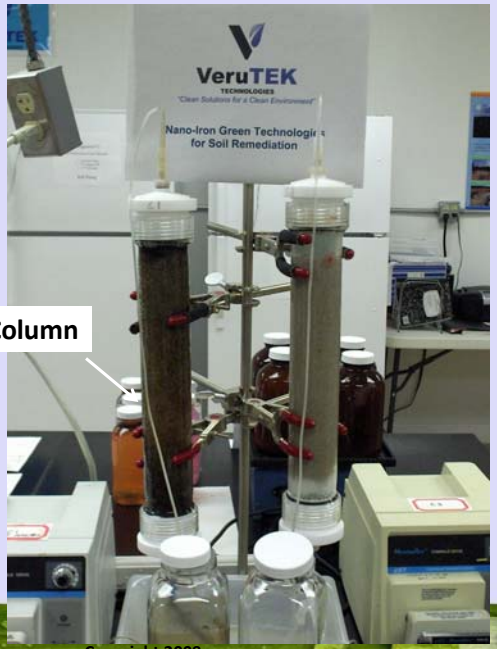


VeruTEK TECHNOLOGIES

Column 2 Collected Effluent Samples
Green Tea Extract with $Fe(NO_3)_3$

VeruTEK TECHNOLOGIES

Comparison of Column 1 Containing nZVI and a Control Column
at Completion of Test - Lemon Balm Extract with $Fe(NO_3)_3$



nZVI Formation in Soil Column

VeruTEK TECHNOLOGIES

Uses and Testing of G-nZVI

- Catalysts
- Reductants
- Comparison to Fe-Chelates
- Probe Compound Examples

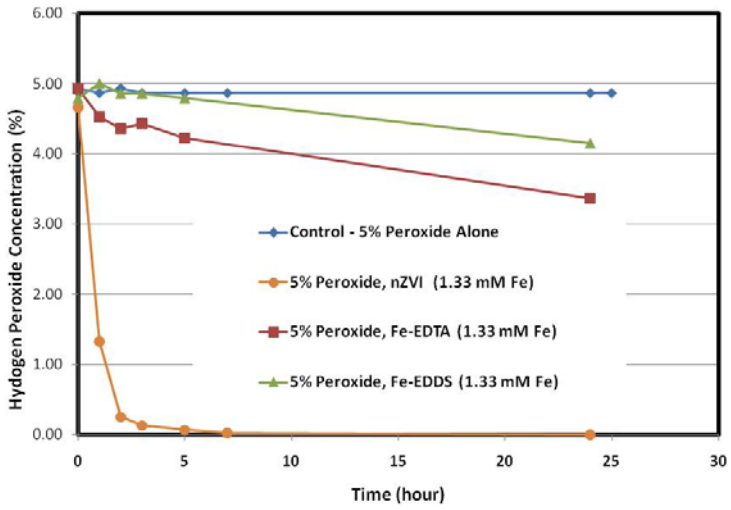
VeruTEK TECHNOLOGIES

Peroxide Catalysis to Promote Radical Formation and Oxidation

- Plant Polyphenol Synthesis of Nano Zero Valent Iron Produces Oxidation Catalysts
- Hydrogen Peroxide is Activated by Nano Zerovalent Iron (nZVI), Fe-EDTA or Fe-EDDS
- Rate Of Peroxide Decomposition Catalyzed With nZVI is Five Times that of Fe-EDTA or Fe-EDDS
- Addition Of VeruSOL™ Slows Down the Rate of Peroxide Decomposition and Acts as a Stabilizer

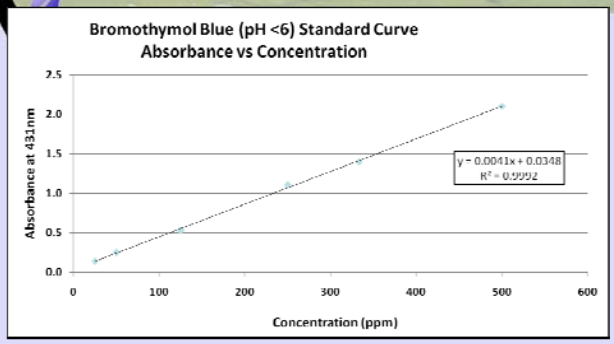
VeruTEK TECHNOLOGIES

Comparison of Hydrogen Peroxide Catalysts



Note: Following synthesis GT-nZVI diluted approx. by factor of 50 prior to use as a catalyst

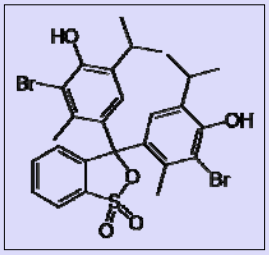
VeruTEK TECHNOLOGIES



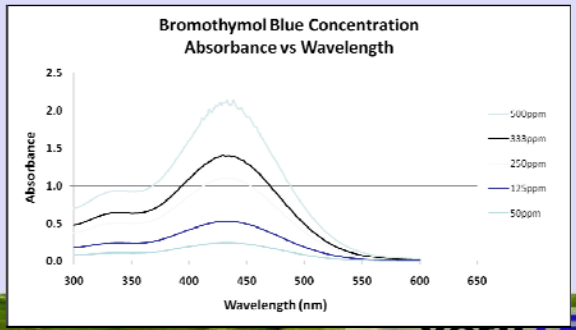
Bromothymol Blue

- Probe Compound
- Only Degrades through Free Radical Pathway

pH <6 pH = 7 pH >7.6

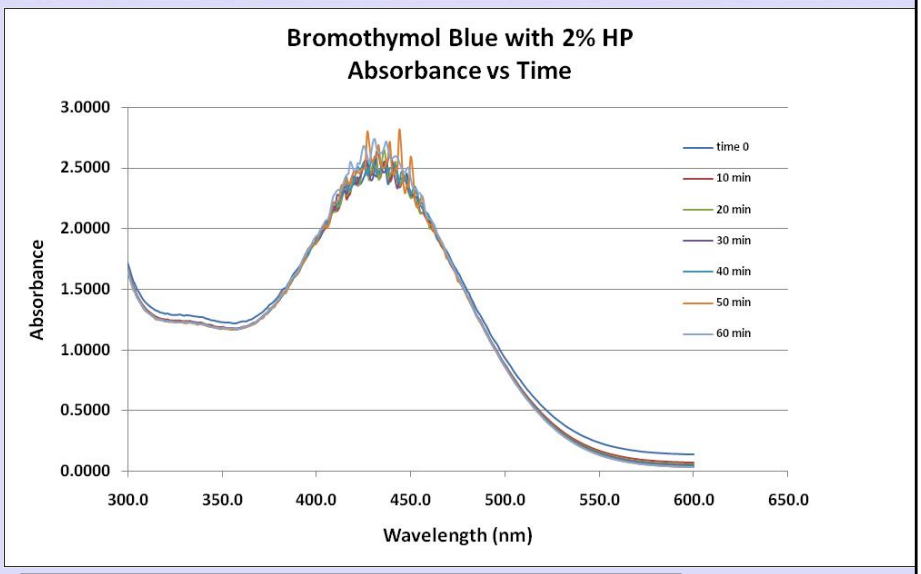


Bromothymol Blue

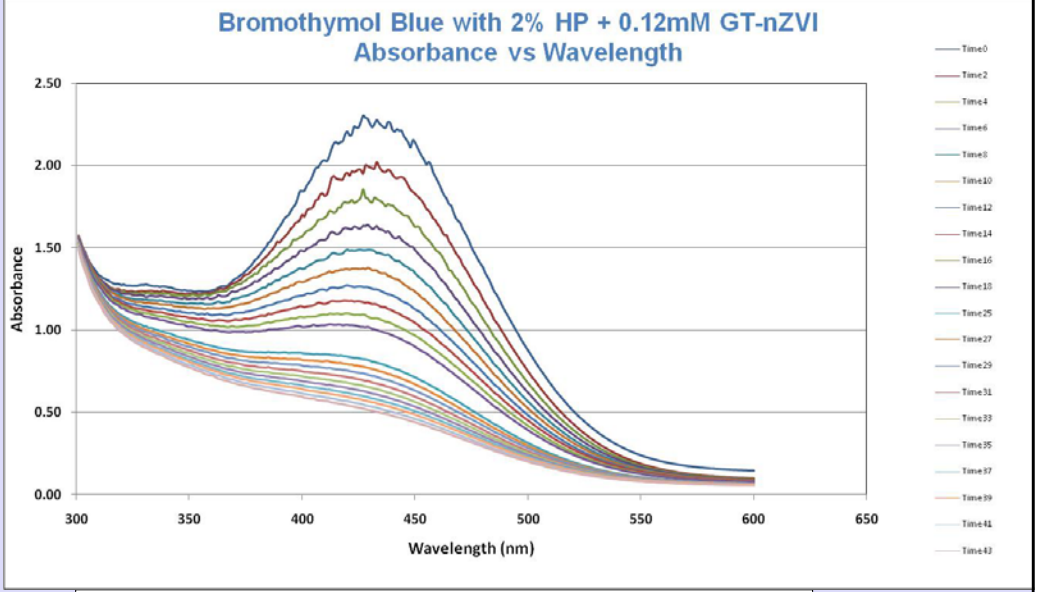


Acidic pH Range

VeruTEK TECHNOLOGIES

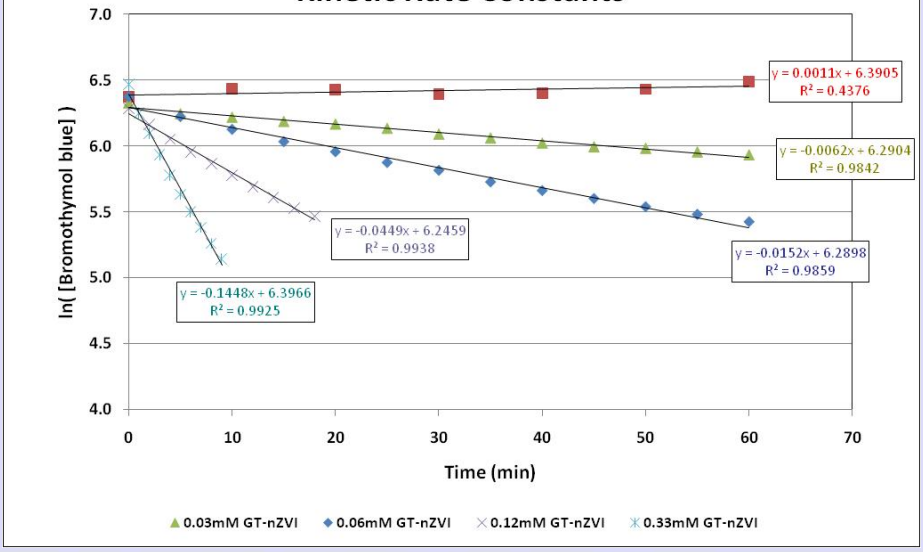


Notes: 1) No Reaction of Uncatalyzed Hydrogen Peroxide (2%) with Bromothymol Blue
2) Initial Bromothymol Blue Concentration = 500 mg/L
3) Bromothymol Blue in the acidic pH range (<6)



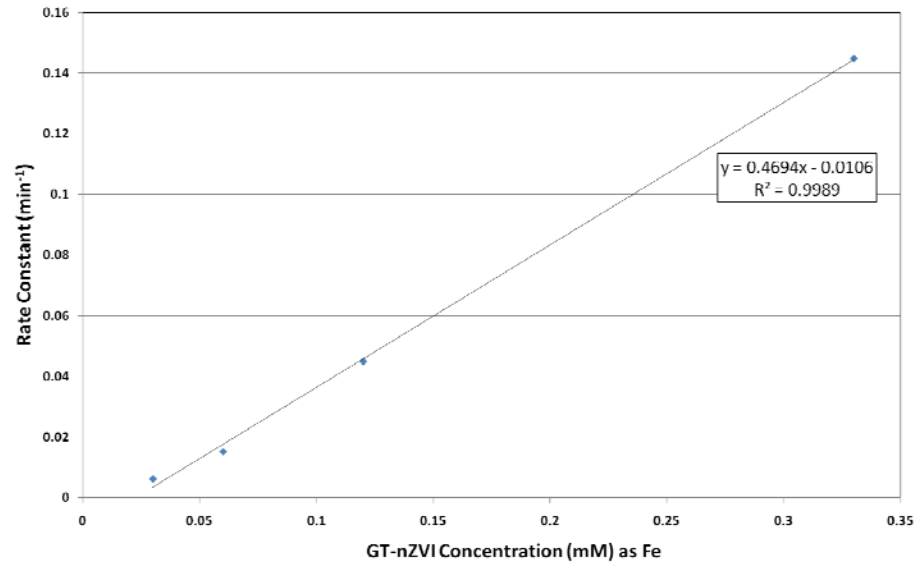
Notes: 1) nZVI Concentration as Fe
2) Initial Bromothymol Blue Concentration = 500 mg/L; acidic pH range (<6)

Green Tea Synthesized nZVI and Bromothymol Kinetic Rate Constants



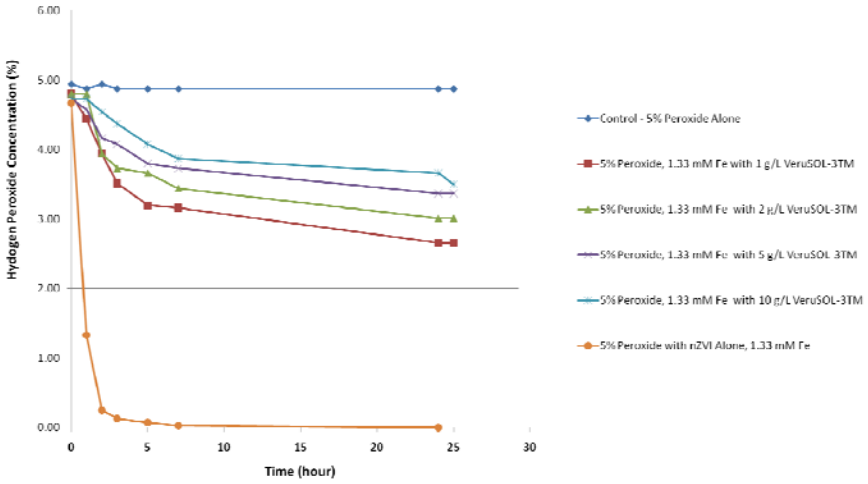
VeruTEK TECHNOLOGIES

Rate of Bromothymol Blue Degradation vs GT-nZVI Concentration with 2% HP



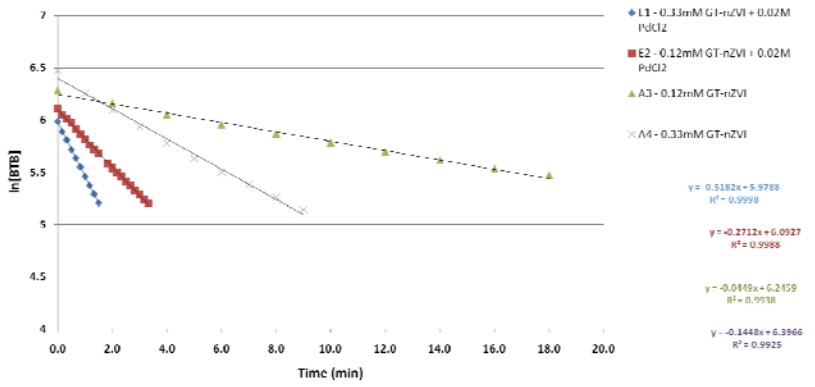
VeruTEK TECHNOLOGIES

Stabilization Effects of VeruSOL-3™ on Decomposition of Hydrogen Peroxide Catalyzed using Green Synthesized Nanoscale Zero Valent Iron



VeruTEK TECHNOLOGIES

Comparison of Bimetallic Pd/Fe Green Synthesized Nano Zero Valent Iron on Bromothymol Blue Degradation with 2% Hydrogen Peroxide



Notes: 1) 0.02 M Pd Cl2 Added After 30 seconds Following Formation of Green Tea synthesized nZVI Particles
2) Pd Coated nZVI Particles Exhibits Faster Reaction Rates than nZVI Particles Alone
3) 6.0 Times Faster Reaction Rate with Pd Coated Particles at 0.12 mM GT-nZVI
4) 3.6 Times Faster Reaction Rate with Pd Coated Particles at 0.33 mM GT-nZVI

VeruTEK TECHNOLOGIES

Use of GT-nZVI as a Reductant

- nZVI and ZVI used Extensively as Reductants
- Initial Work by VeruTEK with GT-nZVI with Chlorinated Solvent Contaminated Soils
- Used for As(III) Sorption/Occlusion with G-nZVI made with Sorghum Bran and $FeCl_3$

VeruTEK TECHNOLOGIES

Soil Columns - Post Iron Loading Before Groundwater Treatment

VeruTEK TECHNOLOGIES

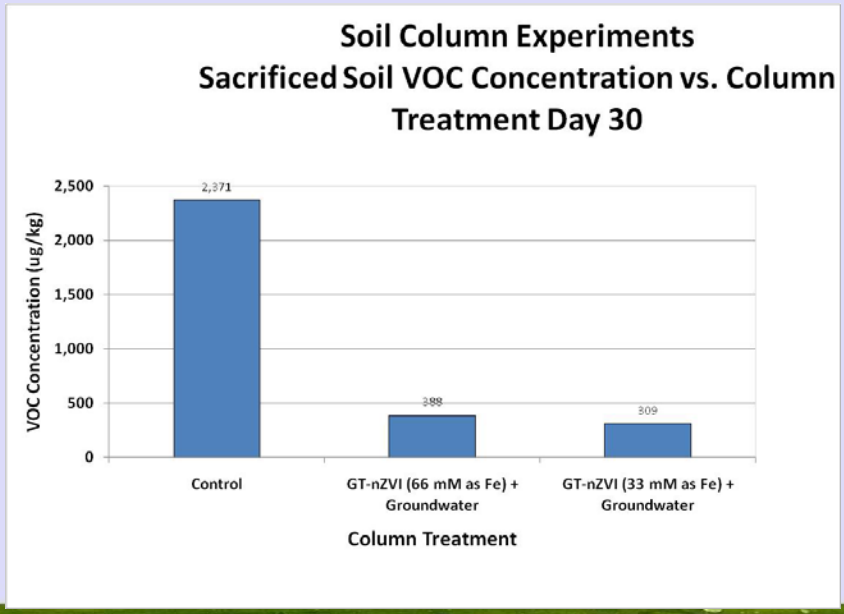
Soil Column 2 (66 mM nZVI) - Post Treatment

VeruTEK TECHNOLOGIES

Soil Column 3 (33 mM nZVI) - Post Treatment

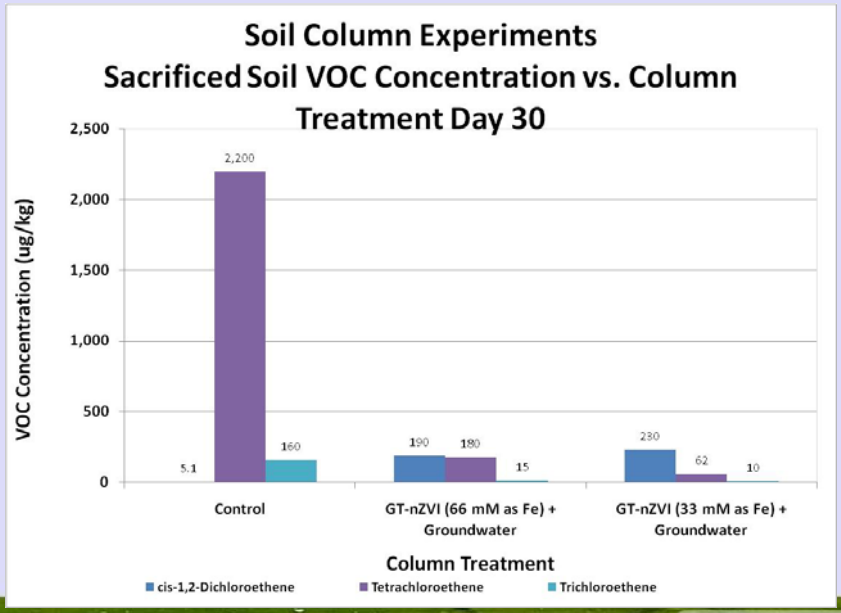
VeruTEK TECHNOLOGIES

Chlorinated VOC Site – G-nZVI Treatment



VeruTEK TECHNOLOGIES

Chlorinated VOC Site – G-nZVI Treatment



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VeruTEK TECHNOLOGIES

Use of GT-nZVI as a Sorbent for As(III)

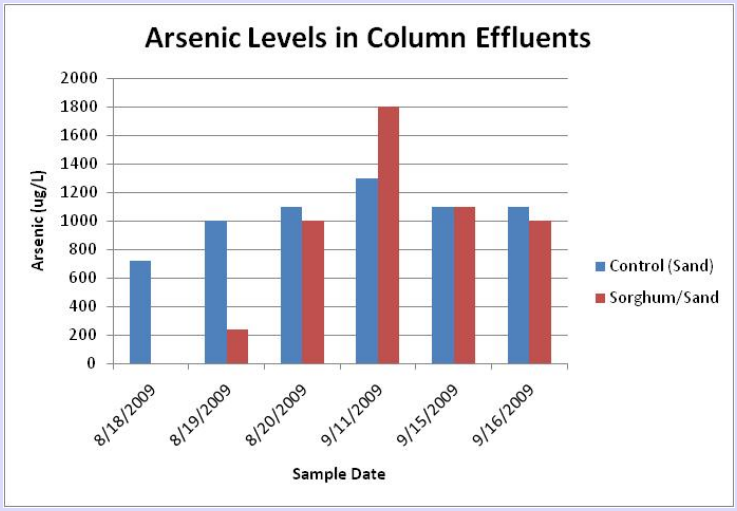
- Used for As(III) Sorption/Occlusion with G-nZVI made with Sorghum Bran and $FeCl_3$

- Soil Column Tests with Control Column (sand only) and Column with a Section of G-nZVI Mixed with Sand at a 75%-25% ratio

- 2.2 cm I.D. PVC Columns, Q = 1.0 mL/min, $Ci_{(AsIII)}$ = 1,000 µg/L, 105.8 cm long columns with 39.7 cm section of G-nZVI/Sand Mixture

VeruTEK TECHNOLOGIES

Arsenic Sorption onto G-nZVI – Column Tests



Samples Taken at 1 L Intervals

82.5 mg As per g of G-NZVI after 2 L of Eluent Passed Through Column

VeruTEK TECHNOLOGIES

Conclusions

- Plant polyphenol-based green synthesis of nanometals works!
- Uses no hazardous materials makes no hazardous wastes
- Polyphenols act as reducing and capping agents
- Many plant extracts can be used including plant wastes
- Polyphenol capping agents slow down reactivity of the nanometals
- Can be used as catalysts for advanced oxidation processes
- Can be used as reductants for reductive dechlorination
- Preliminary work with Arsenic looks promising
- Since nano Fe^0 can be made in presence of VeruSOL™ surfactants incorporating into either O/W or W/O emulsions is possible
- Thanks for coauthors, collaborators, and USEPA

VeruTEK TECHNOLOGIES