SURFACE-MODIFIED IRON NANOPARTICLES
FOR REDUCTIVE DECHLORINATION OF ORGANIC CONTAMINANTS

Štěpánka Klímková, Tomáš Pluhař, Jaroslav Nosek, Vlastimil Antoš, Ondřej Daněk, Lucie Cádrová, Miroslav Černík

stepanka.klimkova@tul.cz, tomas.pluhar@tul.cz, jaroslav.nosek1@tul.cz, vlastimil.antos@tul.cz, ondrej.danek@tul.cz, lucie.cadrova@tul.cz, miroslav.cernik@tul.cz

Technical University of Liberec
Faculty of Mechatronics, Informatics and Interdisciplinary Studies
Institute of Novel Technologies and Applied Informatics
Studentská 2, 461 17 Liberec

ARTEC
Advanced Remedial
Technologies Center

INTRODUCTION

Reductive dechlorination in-situ by zero-valent iron nanoparticles (nZVI) is one of the perspective technologies usable for decontamination of the rock environment polluted by chlorinated organic hydrocarbons [1,2]. Organic compounds are not very soluble in the groundwater and hence classical pump-and-treat technologies for their treatment are not very effective. The principal of the chemical reduction method is substitution of chlorine for hydrogen with consequent contaminant transformation into substantially less toxic non-chlorinated compounds. Application of iron nanoparticles into a system involves the ORP and the pH changes resulting in immobilization of inorganic components including toxic metals caused by reductive precipitation and co-precipitation of mineral or the hydroxides and by adsorption on nanoparticle surfaces [1,3,4].

Figure 1: Structure and decontamination effect of iron nanoparticles [5]

The remediation effects of zero-valent iron are being exploited in the construction of permeable reactive barriers using macroscopic iron filling already for a longer time [6,7]. The advantages of nanoscale zero-valent iron over macroscopic one consist not only in the better reactivity implicit in their great specific surface area of the nanoparticles but also in their transportability in a rock environment. The application of nZVI into the subsurface environment is easier and efficiency of the decontamination process is higher. Nanoparticles can be injected by gravity or under pressure into the sand, silt, fractured rock, fill materials and sediments. The main disadvantage of the present types of nanoparticles is their quite fast surface oxidation in aqueous environment or in the air, which happens unfortunately already during the stage of their storage and application preparation. This oxidation causes not only the loss of a part of the reductive effect of nZVI, but due to the change of particle surface charge, the oxidized particles tend to a higher aggregation and to get stuck on the material whose pores they should be going through. Thereby a relatively significant loss of its transportability in saturated environment occurs.

PROPERTIES OF NANOIRON PARTICLES

Nanoiron particles generally consist of a core composed of a zero-valent iron (Fe0) and a shell of iron oxides, so-called core-shell structure. The surface of nZVI is often being stabilized by a surface active agent. While studying the nZVI it is requisite to take into account that the nanoparticles have different properties than the microscopic iron and these properties markedly depend on their size and their surface state. Iron particles of the size about tens to hundreds nanometres prove specific catalytic, electric and magnetic characters linked with applying the surface phenomena escalating chemical activity of nanoparticle surface atoms. Among iron nanoparticles, particularly the surface unmodified ones, attractive van der Waals, electrostatic and magnetic forces affect, and hence, nZVI aggregates relatively rapidly [8, 9]. On grounds of the great surface nanoparticle area, their surface energy is high and their aggregation tendency is considerable. Aggregate formation rate increases with higher nZVI concentration. Along with the concentration increase, increases also the intrinsic magnetic moment value [9] typical of magnetic material, such as iron and its oxides. The bigger are the aggregates, the stronger is the force they attract other smaller particles to their surface. Unmodified nZVI is adsorbed on material of which pores it should go through, besides the pore plugging caused by big aggregates. This causes significant loss of its transportability through the environment. Aggregate decomposition by ultrasonicating or intensive stirring is possible to a large extent before nZVI application but not more in the surface environment. Also an excessive nZVI reactivity brings complications. While using a very reactive iron reagent, it is necessary to consider the hydrogen release, occurring especially in low pH environment.

STABILIZATION OF NANOIRON PARTICLES

In order to make the real decontamination application more effective, it is necessary to create a stable nZVI dispersion in water solution. On the Technical University of Liberec (TUL), a research with the aim of optimizing the surface properties of accessible nanoiron particles using surfactants, polymers, copolymer, oils and others is under way. Our research has been chiefly focused on nZVI newly produced in a reduction oven from iron oxides in the Centre of Nanomaterial Research (University of Palacky, Olomouc) and presently also commercially on offer. The surface modifier choice is carried out with the aspect of its biodegradability and economical accessibility. It is possible to stabilize nanoiron electrostatically by creating an electrical double-layer, sterically through the use of macromolecules or by their combination - electrosterically.
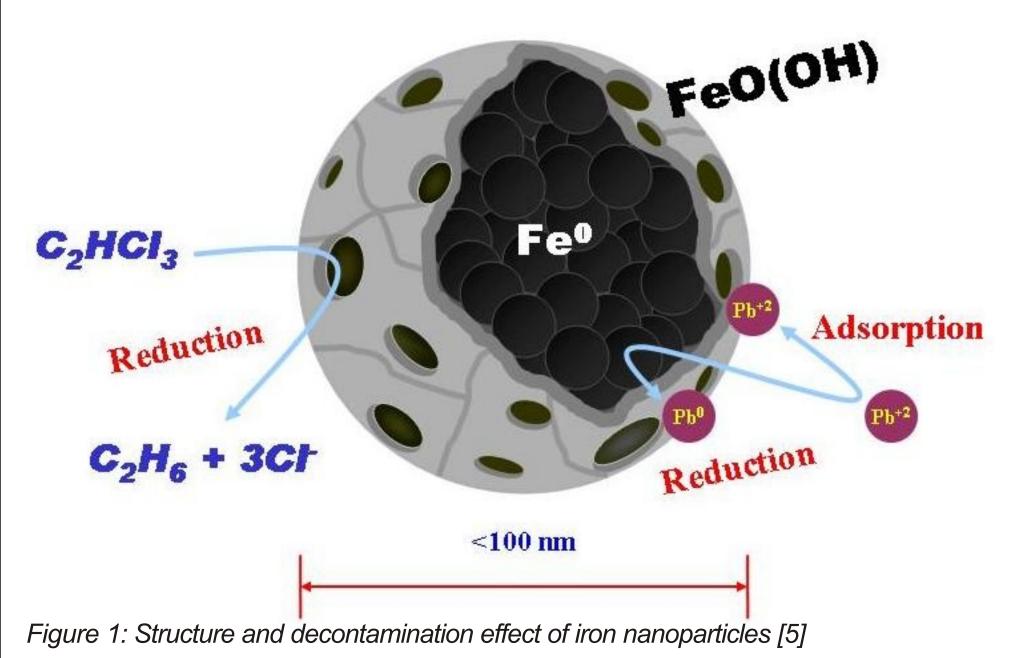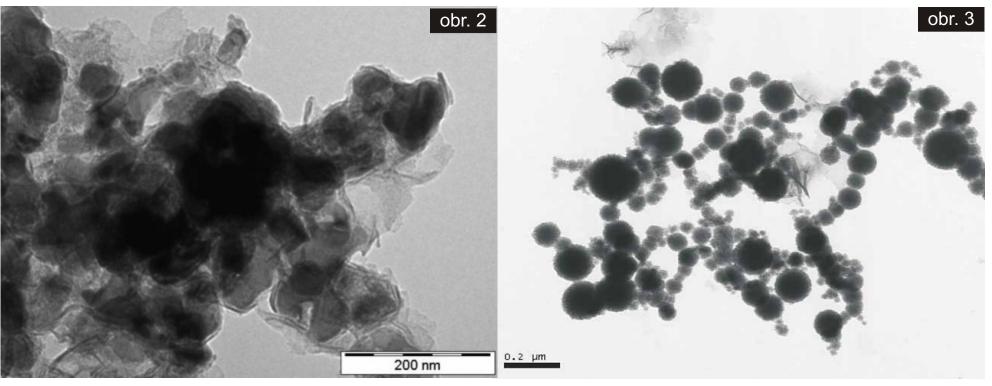
During the surface modification it is important the stabilization agent molecules to be sufficiently soluble in dispersion media and at the same time to be able of a sufficiently firm adsorption on the surfaces of the particles. Protective efficiency depends foremost upon the chemical properties of stabilizer, degree of dispersion, particle electric surface charge, temperature [11] and also ionic strength of the dispersion medium [12].

In the literature, concerning nanoiron particles, findings from researches on optimization of their transportability, dispersibility, reactivity with certain contaminants or stability against undesirable parallel reactions using surfactants as are e.g. Tween 20 and 80 [13,14] and Span 80 [13], polyacrylic acid (PAA) [15,16], triblock copolymers (PMAA-PMMA-PSS) [17,18], Pluronic (EOa-POb-EOa) in combination with oleic acid [19], vegetable oils, starch [20], etc can be found. On the TUL, iron nanoparticles stabilized by surfactants as Tween, salts of polyacrylic acid (Axilat 32A, 32S a 32SV), polystyrenacrylate copolymer (Axilat 2431), further by sodium metasilicate (INHICOR T), starch, carboxymethylcelulose and celulose or their emulsive mixtures with rape oil are tested.

PREPARATION METHODS OF IRON NANOPARTICLES

The nZVI production technique has a significant influence on particle size, shape and chemical composition [21]. There are more ways to produce nZVI. Their summary is listed in the following chart.

Table 1: Preparation methods of nZVI

	Method	Abbreviation	Principle
Chemical methods	Luquid-phase Reduction		Fe^{2+} and Fe^{3+} salt reduction using BH_4^-
	Gas-phase Reduction		thermic reduction of Fe oxides in H_2 atmosphere
	Reverse Micelle; Microemulsion		formation of Fe nano-particlesby reverse micelles micel from Fe^{2+} salts
	Controlled Chemical Coprecipitation		Fe oxide formation in alkaline environment
	Chemical Vapor Condensation	CVC	condensation of Fe particles in controlled atmosphere
	Pulse Electrodeposition		electrolytical reduction of Fe^{2+} salt
	Liquid Flame Spray	LFS	spraying of melt
Physical methods	Inert Gas Conensation	IGC	condensation in inert atmosphere
	Severe Plastic Deformation	SPD	macrostructure deformation low T, high pressure
	High Energy Ball Milling		milling
	Ultrasound Shot Peening	USSP	ultrasonication

In the Czech Republic you can get together with these types of nZVI:
1) **RNIP** (Reactive Nanoscale Iron Particles) are produced by Japanese company Toda Kogyo Corp. This type of nanoparticles with the core of -Fe⁰ and shell created of incompact layer composed of small nanoparticles of magnetite (Fe_3O_4) [22], is delivered in water solution of polyacrylic acid.
2) **Fe^{BH}** is marked nZVI prepared by liquid phase reduction from ferrous or ferric salts ($FeCl_3.6H_2O$ nebo $FeSO_4.7H_2O$) using over-abundance of sodium boron tetrahydride as an reductive agent. Advantage of this nZVI type is quite easy laboratory preparation directly in water solution of surface modifier.
3) Scientest of the Centre for Nanomaterial Research na University of Palacky in Olomouc have developed new types of nZVI **NANOFER**. Nanoparticles are produced by way thermic reductive way from the ferric oxide or from the amorfous ferrihydrite ($Fe_2O_3.nH_2O$) [23]. The size of the nanoparticle including thickness and oxidic layer composition is elected depending on reaction conditions in a reduction oven. The type of precursor and the solution,in which is the produced nanoiron dispersed have the substantial influence. Nowadays some types of NANOFER are also commercially on offer [24].

obr. 2: TEM image of NANOFER 25 produced by NANO IRON, s.r.o.
obr. 3: TEM image of RNIP-10E produced TODA Kogyo Corp.

ANALYTICAL METHODS

The main parameters to be observed concerning the nZVI or their suspensions is their size, shape, chemical composition, surface charge (zeta-potential), dispersion stability and properties of surface active agent solutions. There is a large amount of analytical methods on how to determine these properties and hence their enumeration can not be complete.

For example, for the determination of nanoparticle chemical composition, it is possible to use following techniques:
- X-Ray Photoelectron Spectroscopy (XPS, ESCA)
- X-Ray Diffraction (XRD)
- Mössbauer Spectroscopy
- Raman Spectroscopy
- X-Ray Fluorescence (XRF)
  ...etc

Brief overview of methods on the determination of metal particle size distribution is listed in Table 2.

Table 2: Nanoparticle size distribution methods

Method	Abbreviation	Principle
Dynamic Light Scattering (Quasi-Elastic Light Scattering, Photon Correlation Spectroscopy)	DLS (QELS, PCS)	electromagnetic wave interaction
LASER Doppler Velocimetry (LASER Doppler Anemometry)	LDV (LDA)	aerodynamics, electromagnetic scattering
(Ultra-)Small Angle X-Ray Scattering, Wide Angle X-Raz Scattering	AXS, (U)SANS, WANS	wave interaction
(Ultra-)Small Angle Neutron Scattering, Wide Angle Neutron Scattering	ANS, (U)SANS, WANS	wave interaction
Differential Mobility Analysis	DMA	elektrostatical clasification
Scanning Electron Microscopy (Field Emision SEM)	SEM (FE-SEM)	electron imaging
Transmission Electron Spectroscopy	TEM	electron imaging
Atomic Force Microscopy	AFM	interatomic attraction
Optical Centrifugal Sedimentation, X-Ray Centrifugal Sedimentation	OSC, XCS	sedimentation
X-Ray Gravitational Sedimentation	XGS	sedimentation
Sedimentation Field Flow Fractionation	SdFFF	sedimentation
Gas Adsorption Surface Area Analysis (Brunauer-Emmet-Teller method)	BET	sorption, surface area measurement
Acoustic Attenuation Spectroscopy (Ultrasonic Attenuation Spectroscopy, Ultrasonic Spectroscopy)	AAS (UAS, US)	acoustic wave interaction
Electroacoustic Spectroscopy (Electrokinetic Sonic Amplitude)	ESA	electroacoustic response

On the Technical University of Liberec the efficiency and the kinetics of the reaction of the variously modified nZVI with the certain contaminants is accomplished by way of batch experiments, the transportability in the rock environment by way column experiments. The size distribution of the particles is analyzed by dynamic light scattering (DLS), zeta-potential by combination of laser Doppler velocimetry (DLV) and phase analysis light scattering (PALS) using Zetasizer Nano ZS, Malvern. This instrument also combines static light scattering (SLS) with Debye plot method for polymer molecular weight assessment. For the comparison of the character of different nZVI suspensions, a sedimentation device was also envolved. It is provided by glass cylinder, laboratory scales for monitoring the amount of sedimented particles, camera for to take photos of the dispersion state in selected intervals and computer with own special programs for controlling components and saving all data. Nowadays we are about to monitor magnetic properties of nanoparticles in consequence of their size distribution.

CONCLUSIONS

The particle size analyses confirm the presumption that iron nanoparticles incline to aggregate formation. Using dynamic light scattering, it was found that for example the size of ultrasonicated NANOFER 25S nanoparticles increases in time, namely from 90 nm at the beginning of measuring to c. 400 nm after 80 minutes. According to the so far accomplished sedimentation experiments, nanoparticle surface modified by acrylic acid sodium salt (Axilat 32S a 32 SV) or by polystyrenacrylate copolymer (Axilat 2435) persisted the longest time in uplift. Batch experiments results proved that, compared to the fierce beginning of the reaction of non-surface stabilized particles, the PCE reduction rate through the particles surface modified by these agents slightly lowered, but after all the reaction efficiency is higher. The behavior of nanoparticles during our experiments prompts the fact that for the real nZVI application a more permeable and inert subsurface environment is preferable. The main aim of this research is to optimize this relatively new decontamination technology.

References
[1] ZHANG, W.-x. (2003): Nanoscale iron particles for environmental remediation: An overview. J. Nanopart. Res. 5: 323-332
[2] LIU, Y., MAJETICH, S., TILTON, R., SHOLL, D., LOWRY, G. (2005): TCE dechlorination rates, pathways and efficiency of nanoscale iron particles with different properties. Environ. Sci. Technol. 39: 1338-1345
[3] KANEL, S. R., NEPAL, D., MANNING, B., CHOI, H. (2007): Transport of surface modified iron nanoparticle in porous media and application to arsenic(III) remediation. J. Nanopart. Res. 9: 725-735
[4] XU, Y., ZAO D. (2007): Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. Water Res. 41: 2101-2108
[5] http://gnet.myweb.hinet.net/product2(E).html (Genao Environmental Technology, INC.)
[6] U.S. ENVIRONMENTAL PROTECTION AGENCY (1998): Permeable Reactive Barrier Technologies for Contaminant Remediation; EPA/600/R-98/125; Washington, DC
[7] WILKIN, R. T., CHUNMING, S., FORD, R. G., PAUL, C. J. (2005): Chromium-Removal Processes during Groundwater Remediation by a Zerovalent Iron Permeable Reactive Barrier. Environ. Sci. Technol. 39: 4599-4605
[8] SCHRICK, B., HYDUTSKY, B. W., BLOUGH, J. L., MALLOUK, T. E. (2004): Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. Chem. Mater. 16: 2187-2193
[9] PHENRAT, T., SALEH, N., SIRK, K., TILTON, R.D., LOWRY, G. V. (2006): Aggregation and Sedimentation of Aqueous Nanoscale Zerovalent Iron Dispersions. Environ. Sci. Technol. 41 (1): 284 290
[10] http://ksicht.natur.cuni.cz/serialy/nanocastice/1
[11] NOVÁK, J., et al. Kvapalinák chemie II : skripta. 1st ed. VŠCHT v Praze, 2001. ISBN 80-7080-436-X
[12] Saleh, N., Kim, H.-J., Phenrat, T., Matyjaszewski, K., Tilton, R. D., Lowry, G. V. (2008): Ionic Strength and Composition Affect the Mobility of Surface-Modified Fe0 Nanoparticles in Water-Saturated Sand Columns. Environ. Sci. Technol. 42 (9): 3349-3355
[13] ZHANG, Y., LI, Y., ZIN, Z., WANG, W. (2007): Synthesis of nanoiron by microemulsion with Span/Tween as mixed surfactants for reduction of nitrate in water. Front. Environ. Sci. Engin. China. 1 (4), 466-470.
[14] JOHNSON, J. C., SUN, S., JAFFÉ P. R. (1999): Surfactant Enhanced Perchloroethylene Dechlorination in Porous Media: The Effect on Mass Transfer Rate Coefficients. Environ. Sci. Technol. 33: 1286-1292
[15] KANEL, S. R., CHOI, H. (2007): Transport characteristics of surface-modified nanoscale zero-valent iron in porous media. Water Sci. Technol. 55: 157-162
[16] KANEL, S. R., GOSWAMI, R. R., CLEMENT, T. P., BARNETT, M. O., ZHAO, D. (2008): Two Dimensional Transport Characteristics of Surface Stabilized Zero-valent Iron Nanoparticles in Porous Media. Environ. Sci. Technol. 42: 896-900
[17] SALEH, N., PHENRAT, T., SIRK, K., DUFOUR, B., OK, J., SARBU, T., MATYJASZEWSKI, K., TILTON, R. D., LOWRY, G. V. (2005): Adsorbed Triblock Copolymers Deliver Reactive Iron Nanoparticles to the Oil/Water Interface. Nano Lett. 5: 2489-2494
[18] SALEH, N., SIRK, K., LIU, Y., DUFOUR, B., MATYJASZEWSKI, K., TILTON, R. D, LOWRY G. V. (2007): Surface Modifications Enhance Nanoiron Transport and NAPL Targeting in Saturated Porous Media. Environ. Eng. Sci. 24: 45-57
[19] LAI, J. I., SHAFI, K. V. P. M, ULMAN A., LOOS, K., YONGJAE, L., VOGT, T., LEE W.-L., ONG, N. P. (2005): Controlling the size of magnetic nanoparticles using pluronic block copolymer surfactants. J. Phys. Chem. B, 109 (1), 15-18
[20] HE, F., ZAO, D. (2005): Preparation and Characterization of a New Class of Starch-Stabilized Bimetallic Nanoparticles for Degradation of Chlorinated Hydrocarbons in Water. Environ. Sci. Technol.: 39 (9), 3314-3320
[21] LI, L., FAN, M., BROWN, R. C., VAN LEEUWEN, J. (H.), WANG, J., WANG, W., SONG, Y., ZHANG, P. (2006): Synthesis, Properties, and Environmental Applications of Nanoscale Iron-Based Materials: A Review. Crit. Rev. Env. Sci. Technol. 36: 405-431
[22] NURMI, J. T., TRATNYEK, P. G., SARATHY, V., BAER, D. R., AMONETTE, J. E., PECHER, K., WANG, C., LINEHAN, J. C., MATSON, D. W., PENN, R. L., DRIESSEN, M. D. (2005) : Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry and Kinetics. Environ. Sci. Technol. 39(5): 1221-1230
[23] FILIP, J., ZBORIL, R., SCHNEEWEISS, O., ZEMAN, J., CERNIK, M., KVAPIL, P., OTYEPKA, M. (2007): Environmental Applications of Chemically Pure Natural Ferrihydrite. Environ. Sci. Technol. 41: 4367-4374
[24] http://www.nanoiron.cz/cz/