The effective removal of organic and inorganic contaminants using compositions based on zero-valent iron nanoparticles (n-ZVI)

Efektywne usuwanie zanieczyszczeń pochodzenia organicznego i nieorganicznego za pomocą kompozytów na bazie nanocząstek zero wartościowego żelaza n-Fe(0)

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Abstract: For almost three decades, the engineered nanomaterials (ENMs) due to their reactivity, unique sorption, catalytic, electronic, optical and magnetic properties, have been the subject of extensive research. The results show that these materials can provide a new tool for the remediation of contaminated aquatic ecosystems (surface and groundwater), sediments, soils, military training grounds and waste recycling areas, including electronic waste. In-situ remediation technologies using composites containing metal nanoparticles, mainly zero-valent iron particles (n-ZVI) are becoming more common. The solutions disclosed in numerous publications and patent applications show their applicability, higher effectiveness and lower costs of remediation processes compared to the conventional methods.

Streszczenie: Od prawie trzech dekad inżynierskie nanocząstki (ENM’s, ang. Engineered Nano Materials) ze względu na wykazywaną reaktywność chemiczną, unikatowe właściwości sorpcyjne i katalityczne, elektroniczne, opytczne, magnetyczne są przedmiotem intensywnych badań. Uzyskane wyniki wskazują, że m.in. stanowią one nowe narzędzie do rekultywacji zanieczyszczonych ekosystemów wodnych (wód powierzchniowych i podziemnych), osadów, gruntów, poligonów oraz terenów recyklingu odpadów, w tym elektronicznych. Stosowanie technologii rekultywacji metodą in situ za pomocą kompozytów z udziałem nanocząstek metali, głównie nanocząstek zero wartościowego żelaza n-Fe(0) staje się coraz bardziej powszechnie. Proponowane w licznych publikacjach i patentach rozwiązania wskazują na ich uniwersalność, większą efektywność i niższe koszty realizacji procesu rekultywacji w porównaniu z metodami konwencjonalnymi.
1. Introduction

In previously published review studies we have presented aspects of nanomaterials used in civil and military applications including their origin, structure, unique properties, preparation methods, applicability and aspects related to their environmental release [1-3].

At the beginning of the 1990s, a new innovative technology was developed in the USA to eliminate the environmental impact by using PRBs and other active materials, mostly m-ZVI and μ-ZVI particles [4-22]. The idea behind this technology involves trench excavation (trenching method) perpendicular to the direction of groundwater flow and filling the trenches with a biodegradable slurry (e.g. guar gum based biopolymer as a stabilizer, zeolite-sand mixes) containing suitable ZVI micro- and macroparticles as an active material.

The interaction of the contaminants with the active material is initiated by physical, chemical and/or biological processes, resulting in reduction and/or immobilization [23-31].

The relatively low costs of PRB technology and competitive edge compared to conventional methods: pump and treat, biological reclamation, phytoremediation, activated carbon sorption and others, have made it one of the most commonly used methods [4-23, 30, 31]. Currently in the USA, France, Belgium, Germany, Austria, Italy, United Kingdom, Japan, Canada, Australia, New Zealand and other countries, over a thousand PBR systems are currently in use, and the design, technology and active material are being constantly improved [6, 9, 15, 27-29, 32]. The review of PRB technology by Pawluk et al. [10] has shown that both laboratory and field studies, focused on the practical implementation of this innovative technology, are currently being carried out in Poland.

Many studies have shown that replacing m-ZVI macroparticles and μ-ZVI microparticles with n-ZVI nanoparticles, significantly improves the transformation and detoxification efficiency of many contaminants,
both organic and inorganic, and that those particles are included in the new generation nanomaterials playing a key role in environmental protection [6, 9, 11, 15, 17, 22, 24, 27, 32, 33].

The technologies using zero-valent iron nanoparticle-based nanocomposites, both pure n-ZVI and doped with other metals, referred to as BNPs, are more commonly used in remediation of water ecosystems (ground and surface waters), sediments, waste recycling sites and soils contaminated with toxic and hazardous substances [5-11, 21-37]. They can also be used to decompose high-energy materials (explosives) and their products [38-53] and to deactivate nuclear waste (WA) [54-56]. Degradation and/or immobilization of the contaminants using ENMs is referred to as nano-remediation.

The latest developments in ENMs synthesis and production technology, significantly reduce production costs and allow practical application on a large scale [15, 17, 18, 23-25, 57-61]. So called “green chemistry” processes, which involve replacing iron salt reducing agents incl. NaHB₄, N₂H₄, with eco-friendly water extracts and infusions from natural organic matter in the n-ZVI synthesis, are of particular interest [62, 63]. Highly dispersed metallic particles are more commonly used in the remediation process. However, there are certain concerns related with their release into the environment. This is reflected in the growing number of publications showing the ecological hazards of their application [2, 3, 19, 62, 64-68].

The article presents the factors defining the practical applicability of n-ZVI-based composites, laboratory and field test results on their practical applicability in the contaminant reduction processes, and related hazards.

2. n-ZVI as a component of composites for *in-situ* remediation of water ecosystems, sediments, waste recycling sites and soil

2.1. General considerations

Subjected to extensive laboratory and field studies, n-ZVI particles are of particular interest among metallic nanostructures, due to their potential applications in innovative technologies for degradation of toxic substances in the environment [1-3, 15, 22-24, 29, 32, 69, 70]. The particles show reductive and catalytic properties which classify them as the key ENMs for practical applications in environmental reclamation processes [1, 2, 15, 19, 22-24, 29, 31, 34, 46, 63]. A review of the literature shows that for over 150 years, metallic iron and its oxides were considered as potential active agents in water treatment [71-76]. The developments in nanostructural materials allowed the traditional PRB reclamation methods using m-ZVI and μ-ZVI particles as an active material [6, 9, 12-14, 18, 22, 33], to be updated. With the increase in dispersion rate of n-ZVI, its properties, including the efficiency of contaminant reduction and surface energy (J/m²), change significantly [15, 16, 23, 77]. This was confirmed by numerous research studies which showed a significant increase in the reduction of a wide range of contaminants, including typical contaminants, both organic and inorganic, after replacing ZVI micro- and macroparticles with nanoparticles [16, 23, 26, 32].

In papers on Fe(0) particles presented in literature, „reactivity” and „efficiency” are used interchangeably, which can be confusing because „reactivity” is an intrinsic property of all kinds of a material, but „efficiency” corresponds to its reactivity under given conditions [78]. For Fe(0) particles, it is not possible to directly determine their reactivity, however, the reactivity can be expressed indirectly with the use of a comparative indicator e.g. the value for iodine [79-81]. In [82], a new method of testing of the usefulness of Fe(0) metallic particles in remediation processes in an environment, was proposed. This method relies on the measurement of decoloration in a column of methylene blue (C₁₆H₁₈ClN₃S), which is a triazine derivative NPs of Fe(0), in the form of a suspension (emulsion) in a hydrophobic liquid, are introduced *in situ* by direct insertion into the current of polluted surface water, groundwater, and underground water, as well as into sediments, toxic waste dumps or polluted areas in the ground undergoing decontamination [9], (Fig. 1). This avoids the application of the special construction trenches used in the PRBs’ method, mentioned above [6, 9, 12]. Moreover, in the case of the application of NPs of Fe(0), one can observe a lower degree of the particles’
agglomeration, much higher reactivity and mobility in the medium, as well as allowing it to avoid formation of toxic and carcinogenic by-products, e.g. vinyl chloride (CH\textsubscript{2}=CHCl). The latter was observed during the reduction of organohalogen compounds [83-85]. It should be mentioned that n-\textbf{Fe(0)} particles have a major drawback which relies on their tendency to aggregate relatively quickly, resulting in limitations to the migration distance and finally, in decreasing the effectiveness of their application [1, 15, 16, 27, 28].

![Diagram of organohalogen contaminant mobility in soil: (a) surface soil contaminants (1 – surface soil layer, 2 – surface contamination area, 3 – permeable bed, 4 – bedrock, 5 – low permeability bed, 6 – groundwater, 7 – water intake), (b) contaminant mobility (2a) and DNAPL forming (2b); red arrows in Figures 1(b) and 1(c) indicate contaminant mobility in the soil, (c) LNAPL mobility (2c), (d) groundwater and water intake contamination](image)

\textbf{n-ZVI} granulate is usually used as a composite filler in environmental remediation due to its potential to reduce organic and inorganic contaminants (toxic heavy metal and semi-metal ions) with simultaneous immobilisation (settling) [1, 16, 17, 26-30].

Materials based on zero-valent iron particles, \textit{i.e.} ZVI with different dimensions, are currently available on the market, including three groups of particles [16, 24, 26]:

a) macro (deco-, centi-, milli-) \textbf{m-ZVI} > 500,000 nm (500 \textmu m),

b) micro \textbf{\mu m-ZVI} < 1,000 nm (1 \textmu m),

c) nano \textbf{n-ZVI} \leq 100 nm, with a grain size between 5 and 40 nm.
In recent years, a Canadian company - Golder Associates Inc. is the leader in manufacturing n-ZVI particles using the top-down approach, machining of solid material, grinding or size reduction in SPEX shaker mills (Sample Prep. 8000), Atritter ball mills and XQM planetary ball mills [86]. Large n-ZVI manufacturers include: Toda Kogyo Corp. (Japan), W.-X. Zhang, Lehigh University (USA) and Fischer Scientific (USA).

2.2. n-ZVI synthesis methods

The latest innovations in manufacturing and synthesis of the ZVI particles, allow significant reductions in production costs and an increase in large-scale applications [21, 35, 77, 87-93]. Most nanostructure synthesis methods are based on two opposing approaches which form the basis for different synthesis methods [1, 19, 21, 23, 25, 27, 28, 30, 34-36, 65-67].

2.2.1. Top-down method

The method consists of reducing the size of material (macro-, micro-) to the nano-scale [1, 19-21, 24, 25, 35, 67, 86]. The synthesis methods are relatively straightforward but the disadvantage is a high surface energy of the particles, leading to high susceptibility to aggregation [21, 28, 35, 87]:

a) chemical processes including etching of solid materials using aqueous acid solutions [1, 15, 17, 28, 34, 57, 62, 88];

b) high-pressure magnetron sputtering gas condensation [1, 15, 34, 60, 66].

2.2.2. Bottom-up method

The method is based on the spontaneous combination of single atoms into larger structures “atom to atom”, “particle to particle”, “cluster to cluster” or as a result of controlled nano-crystallite growth:

a) chemical, as a result of:

- Fe(II) and Fe(III) ion reduction, (Equations 1 and 2), usually anhydrous or hydrated chlorides and sulfates(VI) and sodium borohydride (NaBH₄), potassium borohydride (KBH₄), hydrazine (N₂H₄●H₂O) or ascorbic acid (C₆H₈O₆) [1, 7, 15, 17, 19, 23, 26, 30, 34, 90-93]:

\[
2\text{Fe}^{2+}(\text{aq}) + \text{BH}_4^-(\text{aq}) + 3\text{H}_2\text{O}(\text{aq}) \rightarrow 2\text{Fe}^0(\text{s}) + \text{H}_2\text{BO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{H}_2(\text{g})
\]  

(1)

\[
4\text{Fe}^{3+}(\text{aq}) + 3\text{BH}_4^-(\text{aq}) + 9\text{H}_2\text{O}(\text{aq}) \rightarrow 4\text{Fe}^0(\text{s}) + 3\text{H}_2\text{BO}_3^-(\text{aq}) + 12\text{H}^+(\text{aq}) + 6\text{H}_2(\text{g})
\]  

(2)

- geothite [α-FeO(OH)] reduction using dihydrogen (H₂) [21, 28, 35, 94],

- hydrolysis (Equation 3) and condensation (Equation 4) of precursors, usually metal (Al, Ti) and silicate (Si) alkoxides with a general formula M(OR)ₙ, where R-alkyl, referred to as a sol-gel is used to form crystalline and amorphous nano-oxides [21, 35, 95-98]:

\[
\text{MOR} + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{ROH}
\]  

(3)

\[
\text{MOH} + \text{ROM} \rightarrow \text{M-O-M} + \text{ROM}
\]  

(4)

- reversed micelle method (microemulsion) [28, 35, 99],

- metal ion reduction using ultrasound – sonochemical reduction [12, 28, 35, 87],

- metal ion reduction using UV radiation – photochemical reduction [12, 21, 28, 35, 100-104],

- hydrothermal synthesis [12, 18, 21-24, 35, 67, 81, 87, 89, 105-107],

- electrochemical deposition [21, 27, 28, 31, 85, 108],

- chemical vapour phase deposition, CVD, [21, 28, 29, 35, 74].
b) biological, with the following used as Fe(II) and Fe(III) ion reducing agents:

- extracts or infusions from plant leaves or shoots (see Table 2) for obtaining iron nanoparticles characterized by a lower agglomeration rate, referred to as BB-Fe NPs, as opposed to the particles obtained by chemical reduction, referred to as n-ZVI [21, 35, 90, 92, 103, 108-112]. The extracts and infusions are the reducing agents used in “green chemistry” and may be used to replace sodium borohydride (NaBH4), potassium borohydride (KBH4) and hydrazine (N2H4·H2O) – hazardous substances commonly used as reducing agents [12, 21, 35]. Table 1 shows the plant materials commonly used in extracts and water infusions and the microorganisms used as iron salt reducing and stabilizing agents for the n-ZVI particles.

The iron salt reducing agents and stabilizing agents for metallic nanostructures include natural substances occurring in bottom fermentation beers including: maltose (C12H22O11), dextrins (complex hydrocarbons), lactic acid (C2H4OHCOOH), polyphenols and alanines [α-aminoacids –[CH2CH(NH2)COOH] [90, 92, 103, 113, 114].

| Plant material                                | Microorganisms      |
|-----------------------------------------------|---------------------|
| American blueberry (lat. Vaccinium corymbosum) (leaves and shoots) [35, 90, 108, 110, 115] | Bacteria [35, 90, 92, 108, 120, 121] |
| Oak (leaves) [35, 90, 92, 108, 110]           | Viruses [35, 90, 108, 110, 112] |
| Mulberry (leaves) [35, 90, 92, 108, 110]      | Viruses [35, 90, 108, 110, 112] |
| Cherry (leaves) [35, 90, 92, 108, 110]        | Viruses [35, 90, 108, 110, 112] |
| Green tea (leaves) [90, 92, 108, 110, 116, 117] | Fungi [90, 110, 122-125] |
| Fenugreek (lat. Trigonella foenum-graecum) [90, 108-110, 118] | Fungi [90, 110, 122-125] |

- essential oils [90, 92, 108, 110, 112],
- biodegradable plant surfactants [90, 108, 110, 125].

Generally, all plant-based materials are environmentally friendly and increase the compatibility of derived nano-materials, as observed in the synthesis of gold nanoparticles [90, 92, 103, 108, 109, 111, 114, 117].

c) physical, as a result of:

- microwave radiation [21, 35, 126],
- high pressure magnetron sputtering gas condensation [21, 29, 35],
- ablation (cooling) metallic iron vapours using laser radiation (laser ablation) [127],
- arc discharge [27, 28, 35, 128].

n-ZVI particles can be obtained by the thermal reduction of zero-valent iron pentacarbonyl, Fe(CO)5 in organic solvents or argon. High synthesis costs and significant amounts of effluent make this method impracticable [78]. The high potential for practical application of n-ZVI and ZVI-based composites led to a number of research projects aimed at developing new synthesis routes and determining their chemical composition [31, 35, 89, 90, 129].

2.3. n-ZVI structure (morphology) and chemical composition

Testing has shown that the structure, dimensions, shape, particle size distribution and chemical composition of ZVI depends on the synthesis route and conditions, substrates used and the atmosphere in direct contact with the particles [28, 29, 31, 92, 93, 104, 130-134]. The findings were verified by the specification of ZVI particles available on the market and detailed in Table 2.
Table 2. Properties of ZVI particles offered by different manufacturers

| Manufacturer                              | Synthesis methods | ZVI particle size | Chemical composition of the coating                  |
|-------------------------------------------|-------------------|-------------------|------------------------------------------------------|
| Toda Kogyo Corp. (Japan)                  | H₂ reduction      | 70 nm             | Magnetite, (Fe₃O₄)                                   |
| W.-X. Zhang, Lehigh University, (USA)     | NaBH₄ reduction   | 10-100 nm         | Geothite, [FeO(OH)], Wustite, FeO                   |
| Fischer Scientific (USA)                 | electrolytic      | 150 µm            | α-ZVI                                                |

A detailed morphology and structure of ZVI particles was developed using the latest research methods:

a) Transmission Electron Microscopy (TEM) [93, 130, 135, 136],

b) Scanning Electron Microscopy (SEM) [93, 136, 137],

c) Scanning Transmission X-ray Microscopy (STXM) [130],

d) Brunauer-Emmett-Teller surface area measurement (BET-N2) [35, 93, 130, 134, 137],

e) X-ray Diffraction (XRD) [93, 130, 134, 137-139],

f) Energy Dispersive X-ray spectrum (EDX) [130],

g) X-Ray Photo-electron Microscopy (XPS) [93, 130, 140-142],

h) Electron Energy-Loss Spectroscopy (EELS) [136],

i) Fourier Transform Infra-Red Spectroscopy (FT-IR) [35, 137],

j) Electro-Migration Nanoparticles (EMNP) [31, 34, 35],

k) Mössbauer Spectroscopy (MS) [138, 143, 144],

l) Iso-Electric Point (IEP) [93],

m) Tomographic Reconstruction (TR) [35, 139].

Results of the tests show that ZVI particles made using the bottom-up method usually feature a core-shell passivating oxide layer structure [21, 28, 29, 35, 143, 145, 146]. The core is made up of the iron atoms in their alpha allotropic form (α-Fe) which, in the ambient conditions, is stable and show ferromagnetic properties [35, 136, 147-154]. The interaction of different oxygen forms (●O, O₂, O₃, H₂O₂) and H₂O with the surface of primary α-ZVI particles leads to the formation of a passivating oxide layer [35, 136, 146, 148, 151-154]. Elemental iron ZVI is an electron donor and slowly oxidizes to Fe(II) ions releasing 2e⁻ (Equation 5):

\[ \text{Fe(0)}(\text{s}) \rightarrow \text{Fe(II)}(\text{aq}) + 2e_\text{(aq)}^- \]  \hspace{1cm} (5)

The main component of the passivating oxide layer is an oxidized Fe(II) layer containing: Fe(II)O, Fe(III)(OH)₃, Fe(II)Fe(III)₂O₄. The complete oxidation of those products generates geothite [iron(III) hydroxy-hydroxide Fe(III)O(OH)) and iron(III oxy-hydroxide [Fe₃(III)O₄·0.5H₂O] [148, 154]. Fe(II) and Fe(III) ions on the ZVI surface make the passivating oxide layer insoluble in the neutral environment, protecting the primary ZVI particles against sudden oxidation [35, 145-150]. The ZVI particle corrosion rate shows that it to be dependent on the raw material, reducing agent and te medium’s pH. At pH 8.9-6.5, the corrosion rate decreases, whereas at pH 6.5 it is constant (100% ZVI content is maintained) [35, 136, 151-154]. Figure 2 shows the zero-valent iron ZVI nanoparticles (grains) with the core-shell passivating oxide layer [35].
Figure 2. ZVI nanoparticles (grains) with the core-shell passivating oxide layer: a) αZVI, b) FeO, c) Fe(OH)$_2$, d) FeO·Fe$_2$O$_3$, e) FeOOH, f) Fe$_2$O$_3$·0.5H$_2$O

Figure 3. Electron microscope (SEM) images of the ZVI particles: (a) agglomerate 200 nm in diameter with 10 nm grains (Photo (b)) (Photo by Z. Foltynowicz)

SEM images (Fig. 3) shows the nanoparticle structure, a key factor in determining reactivity. Particles in the nanoscale (1-100 nm) region show a large surface area available for the interaction with reagents resulting in a high reactivity of their surfaces. Iron nanoparticles, 1 to 100 nm in diameter and specific surface area from 20 to 40 m$^2$/g, show 10 to 1,000 times higher reactivity than granulated iron particles with a surface area below 1 m$^2$/g. The surface area of the spheres increases by a factor of 10, while the particles’ diameter decreases by a factor of 10. Iron powder with a particle diameter of 10 nm instead of 10 μm will show a 1,000 times higher specific surface area. The oxidation rate of ZVI particles is significantly higher than the oxidation rate of iron powders with a diameter of several micrometres and shows a different mechanism, since unlike microparticles, it does not require water or moisture to be active (Equation 6) [155, 156]:

$$5Fe + 7/2O_2 \rightarrow Fe_2O_3 + Fe_3O_4 \quad (6)$$
Nanoparticles show a very high specific interaction between the internal particles and surface particles due to the relatively small radius of the spherical forms or the dimensions of other forms, resulting in “compression” of the surface structures, hence the unique hardness of nanomaterials. The particles are thermodynamically unstable and tend to interact and react in order to increase the distance between them. The passivating layer has a porous structure, thanks to which the nanoparticles can bind trace amounts of metals: Pt, Pd, Ag, Au, Ni resulting in further increasing their reactivity [21-25, 27, 35, 155-157].

2.4. Stabilizers (emulsifiers) of engineered nanoparticles

The passivating core layer of the ZVI particles provides active centres for chemical complexes, *i.e.* chemical adsorption on its surface determining the nanoparticle efficiency in the remediation processes [20-25, 27, 78, 97, 103]. Small particle size, electrostatic intermolecular van der Waals forces and magnetic interactions, result in a significant tendency to aggregation and sedimentation [6, 18-27, 30, 97, 103, 131]. To limit this tendency, the ZVI surface is doped with different substances, including stabilizing emulsifiers, *e.g.*, chelating agents, EDTA, NTA, which significantly increase the lifetime of colloidal solutions. Table 3 shows the example materials used to stabilize the nanoparticles.

Table 3. Protective coatings used as stabilizing agents (emulsifiers) for ENM emulsions

| Chemical composition of the composite | Emulsifier | Ref. |
|--------------------------------------|------------|-----|
| Primary n-αZVI particles             | Hydrophilic biopolymers: | |
|                                      | a) plant polysaccharides including: | |
|                                      | – starch (C₆H₁₀O₅)n, linear chain, amylose | [158, 159] |
|                                      | – dextran sulphate | [22, 160] |
|                                      | – guar gum | [35, 161] |
|                                      | – alginates, alginic acid calcium or sodium salt | [162] |
|                                      | – diacetylquinine (C₅₆H₁₀₃N₉O₃⁹) | [22, 23, 35, 163-165] |
|                                      | – cellulose derivative: carboxymethyl cellulose, CMC; | [166-169] |
|                                      | b) chitosan, chitin derivative | [35, 170, 171] |
| n-Fe₃O₄(FeO•Fe₂O₃) (magnetite)      | Dippeptide ethyl ester (C₁₄H₁₈N₂O₅), aspartame, Asp-Phe-OMe | [21-23, 35] |
|                                      | Polyelectrolytes (flocculating agents), natural and synthetic: | |
|                                      | – polyacrylic acid, PAA, | [21, 35, 172-177] |
|                                      | Natural oil-based microemulsions | [21-25, 35, 178] |
|                                      | Amphiphilic compounds including surfactants (cationic, anionic, non-ionic) | [21-25, 35, 179-189] |
| Doped primary n-ZVI particles (bimetallic BNPs) | Xanthan gum gels: | [21, 35, 184] |
|                                      | Phospholipids – (phosphatidylcholines), *e.g.*, lecithin | [12, 35, 185] |
|                                      | Natural organic matter (NOM) including humic acids (HA) | [21-25, 35, 186, 187] |

2.5. ZVI particle carriers

ZVI particles, when applied on suitable materials, often show higher efficiency, stability and applicability in environmental remediation [21-23, 35, 188]. Table 4 shows the stabilizers used in the production of effective ZVI-based composites.
Table 4. Materials used as n-ZVI carriers

| Nanocomposite | Carrier                                                                 | Ref.                   |
|---------------|-------------------------------------------------------------------------|------------------------|
| n-ZVI/C       | Anionic hydrophilic carbon suspended in PAA                             | [21-25, 35, 103, 189]  |
| n-ZVI/EG      | Exfoliated graphite (EG)                                               | [89, 103, 190, 191]    |
| n-ZVI/OMC     | Ordered mesoporous carbon (OMC)                                        | [21, 35, 192-195]      |
| n-ZVI/GC      | Granulated active carbon (GC)                                          | [103, 112, 170, 171, 196-199] |
| n-ZVI/SiO<sub>2</sub> | Mesoporous silica (SiO<sub>2</sub>)                              | [35, 97, 103, 200-202]  |
| n-ZVI/chitosan | Chitosan                                                               | [35, 103, 200]         |
| n-ZVI/R       | Resins:                                                                | [35, 103]              |
| n-ZVI/PR      | – polystyrene resins (PR).                                             | [103, 203-207]         |
| n-ZVI/ER      | – ion-exchange resins.                                                 | [35, 103, 208]         |
| n-ZVI/CM      | Clay materials (CM) including:                                         | [103, 209, 210]        |
|               | – bentonite                                                            | [103, 211, 212]        |
|               | – montmorillonite                                                     | [35, 213, 224]         |
|               | – mica                                                                 |                        |
|               | – kaolin clay                                                          |                        |
| n-ZVI/pumice   | Pumice                                                                 | [35, 88, 103, 215]     |
| n-ZVI/MG      | Metallic glass, amorphous metal and non-metal alloy                    | [35, 94, 103, 216-223] |
| n-Fe/polymer  | Stabilizing polymers                                                   | [224-226]              |
| n-ZVI/GO      | Graphene oxide                                                         | [227-230]              |
| n-ZVI/MWCNTs  | Multi-walled carbon nanotubes (MWCNTs)                                 | [230-232]              |
| n-ZVI/LDHs    | Layered double hydroxides (LDHs)                                       | [231-233]              |
| n-ZVI/NMOs    | Nano-sized metal oxides (NMOs)                                         | [94, 103, 234-235]     |
| n-ZVI/zeolite | Zeolites                                                               | [212]                  |

3. Factors determining chemical efficiency of ZVI particles

Many publications show that the synthesis routes and conditions, substrates, reducing agent, suitable protective coating, carrier or doping with other metals used in ZVI synthesis, have a significant effect on many parameters determining its reactivity [8, 10, 20-25, 27-30, 94, 103, 215]. Due to the role played in the remediation processes, the following factors are of key importance:

a) **ZVI particle shape and size** [27, 97, 103, 118, 236-240]: The dimensions of nanoparticles referred to in the literature are between 10 and 100 nm.,

b) **ZVI particle size distribution** [241],

c) **pH of the colloidal ZVI suspension** [236, 242]: pH is a key factor affecting the effectiveness of nanoparticles in contaminant degradation processes – the processes run faster in an acidic environment (pH 4) than in an alkaline environment (pH 8.1), as shown in the example of nitrobenzene reduction with ZVI particles [242],

d) **ionic strength of the colloidal ZVI suspension** [103, 165, 236],

e) **chemical stability of the ZVI particle surface area** [57, 89, 176, 187, 213, 243-246],

f) **ZVI particle mobility (transport)** is determined by the following factors:

   - charge and spatial orientation of the emulsifier particles [97, 103, 162, 174, 184, 247, 248],
   - limited stabilization of the colloidal ZVI suspension [97, 103, 147, 236, 248, 249],
   - intermolecular interaction [147, 236],
   - nanoparticle-media type interaction [147, 179, 236, 250],
   - affinity to the dense non-aqueous liquid phase DNAPL, [36, 216, 220, 236, 242, 250, 251],
   - ionic strength and chemical composition of the ZVI/H<sub>2</sub>O system [36, 252],
   - ZVI aggregation rate [97, 104, 216, 220, 236, 252],
   - natural organic matter in the NOM system [97, 103, 253];

g) **operating parameters** (dimensions, particle size distribution, additives, chelating agents and carrier, chemical composition of the dispersing medium, composite effectiveness) affecting the effectiveness of ZVI particles [254].
4. Metallic binary nanoparticle systems

The high porosity of ZVI nanoparticles means they show a tendency to bond trace amounts of metals including platinum (Pt), palladium (Pd), silver (Ag), gold (Au), nickel (Ni), copper (Cu) which in practice increases their reactivity [27, 35, 97, 103, 262]. The nanoparticles of one type of metal doped with another metal in the amount of 0.1 wt.%, are referred to as the BPNs [35, 103] which, due to their effectiveness in contaminant reduction, are classified as a new category of innovative active materials, used more and more frequently in ecosystem remediation technologies [35, 158, 262].

Table 5. Example binary metallic systems of BNP nanoparticles showing potential for reducing contaminants

| Chemical composition of the bimetallic system | Reduction | Ref. |
|---------------------------------------------|-----------|------|
| n-Fe/Pt                                     | Hydrocarbon dehalogenation | [97] |
| n-Fe/Ag                                     | NO₃ reduction | [103] |
| n-Fe/Pd/amphiphile                          | Trichlorobenzene dehalogenation | [179] |
| n-Fe/Pd/starch                              | Dehalogenation: TCE, PCB – (see 5.2) | [170, 184] |
| n-Fe/Pd/CMC                                 | Trichloroethylene dehalogenation | [166] |
| nFe/Pd/SiO₂                                 | Trichlorobenzene dehalogenation | [170] |
| n-Fe/zeolite                                | Explosives biodegradation | [235] |
| Fe/Au                                       | Reduction: NO₃ | [263, 264] |
| Fe/Ni                                       | Tetrachloroethane degradation, phenol biodegradation | [256, 257] |
| Fe/Cu                                       | NO₃ reduction | [27, 263, 264] |

Studies on tri-metallic systems, e.g. ZVI/ PdCu/Ni for removing diclofenac, used to relieve pain from the water environment [155], are appearing more frequently in literature.

5. ZVI’s mechanism of action

5.1. General

Free common metals, including ZVI, show a high affinity for all forms of oxygen and water, and thus a natural susceptibility to return to the combined state. As a result, achieving a state of equilibrium with the environment results in products of that interaction forming on the metal surface. The reaction for common metals is generally referred to as corrosion (or rusting in case of iron) [84, 92, 93, 97, 100, 103, 107, 140, 146-149, 264, 265]. Metallic ZVI is a moderate reducing agent which reacts with dissolved oxygen (O₂) (DO) and to some degree with water, as demonstrated by the following simplified corrosion reactions (Equations 7 and 8) [84, 264, 265]:

\[
2\text{Fe}(0)(s) + 4\text{H}^+ + \text{O}_2(aq) \longrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O} \quad (7)
\]

\[
\text{Fe}(0)(s) + 2\text{H}_2\text{O}(aq) \longrightarrow \text{Fe}^{2+} + \text{H}_2(g) + 2\text{OH}^- \quad (8)
\]

The reaction rate can be increased or decreased by changing the chemical composition of the solution and/or the chemical composition of the metallic component [35, 264].

The corrosion reactions show that ZVI is an electron donor which slowly oxidizes to Fe(II) ion with the release of 2 e⁻ (Equations 9-11):

\[
\text{Fe}(0)(aq) \longrightarrow \text{Fe}^{2+}(aq) + 2e^- \quad (E_0 = -0.44 \text{ eV}) \quad (9)
\]

\[
\text{Fe}^{2+}(aq) \longrightarrow \text{Fe}^{3+}(aq) + e^- \quad (E_0 = -0.77 \text{ eV}) \quad (10)
\]
The corrosion mechanism can also be described as a Heusler mechanism reaction (Equations 12 and 13):

\[ \text{Fe}(0) + \text{H}_2\text{O} \rightarrow (\text{FeOH})_{\text{ads}} + \text{H}^+ + \text{e}^- \]  \hspace{1cm} (12)

\[ \text{Fe} + \text{OH}^- \rightarrow \text{FeOH}^+ + 2\text{e}^- \] \hspace{1cm} (13)

or the Bockris mechanism reaction (Equations 14 and 15):

\[ (\text{FeOH})_{\text{ads}} \rightarrow \text{FeOH}^+ + \text{e}^- \] \hspace{1cm} (14)

\[ \text{FeOH}^+ + \text{H}^+ \rightarrow \text{Fe}(\text{II}) + \text{H}_2\text{O} \] \hspace{1cm} (15)

The electrons released in the ZVI reduction process neutralize H\(^+\) ions in water forming dihydrogen which in turn reacts with atmospheric oxygen, forming water (Equations 16 and 17):

\[ \text{Fe}(0) \rightarrow \text{Fe}(\text{II}) + 2\text{e}^- \] \hspace{1cm} (16)

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}^* + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} \] \hspace{1cm} (17)

The metallic ZVI particles are moderate reducing agents which react with dissolved oxygen to a certain degree prescribed by the chemical composition of the water – a reaction used to reduce various contaminants in water and soil.

The corrosion process seems very complex which is reflected by the chemical composition of the metallic ZVI surface making it difficult to determine the actual mechanism. It is generally accepted that it follows a charge transfer reaction [265]. Fe(II) ions on the surface of metallic ZVI oxidize to Fe(III) ions or other oxides: FeO\(_{0.95}\), FeO·OH, Fe\(_2\)O\(_3\), [Fe(II)Fe(III)\(_2\)O\(_4\)] [35, 97, 103, 264-267]. Since the oxides forming on the ZVI surface do not form a cohesive protective layer, the corrosion process is relatively slow [21, 97, 103].

### 5.2. Organic matter degradation

In the case of organic contaminants, electrons released by the ZVI nanoparticles initiate the reactions leading to their reduction (defragmentation) to neutral products, which may include:

a) \text{beta-elimination}, by forming partially dehalogenated short-life intermediate products which in turn are converted into simple hydrocarbons including tetrachloroethene, TCE, or ethene (C\(_2\)H\(_4\)) [268-270],

b) \text{hydrolysis} or \text{gradual degradation}, where a single chlorine atom is removed at each stage and the final products are simple hydrocarbons, like ethane (C\(_2\)H\(_4\)), ethene (C\(_2\)H\(_6\)) etc. [83, 97, 103, 271-275],

\[(\text{Equations 18 and 19}): \]

\[ \text{RCl} + \text{H}^+ + 2\text{e}^- \rightarrow \text{RH} + \text{Cl}^- \] \hspace{1cm} (18)

\[ \text{Cl}_2\text{C}=\text{CCl}_2 + \text{H}^+ + n-\text{Fe}(0) \rightarrow \text{C}_2\text{H}_4 + 4\text{Cl}^- + \text{Fe}(\text{II})/\text{Fe}(\text{III}) \] \hspace{1cm} (19)

Contaminants such as polychlorinated biphenyls (PCBs) or polychlorinated benzenes are reduced to their corresponding hydrocarbons [83].
5.3. Reduction/immobilization of inorganic matter

ZVI shows an ability to reduce and absorb elements, as demonstrated in many laboratory and field studies [39, 142, 276-289]. The reduction of heavy metal ions formed in contact with n-ZVI or n-ZVI-based composites, may follow two different mechanisms:

a) firstly, where the reduction results from direct contact with n-ZVI [35, 279, 283], (Equation 20):

\[
\text{Fe}(0) + \text{Me}^{n+} + e^{-} \rightarrow \text{Fe}^{(II)} + \text{Me}^{(n-x)^+}
\] (20)

b) secondly, where the heavy metals are absorbed onto the n-ZVI core-shell surface and are subsequently reduced by Fe(II) ions released by the ZVI core [35, 264, 279]. Most heavy metals can have an intermediate oxidation state and are gradually reduced to the zero oxidation state [283], (Equation 21):

\[
\text{Fe}(0) + \text{Me}^{n+} + e^{-} \rightarrow \text{Fe}^{(II)} + \text{Me}^{(n-1)^+} + e^{-} \rightarrow \text{Fe}^{(II),(III)} + \text{Me}^{(0)} + e^{-}
\] (21)

6. Methods of increasing the efficiency of contaminant degradation using n-ZVI particles and the biogenic approach

It has been found that the n-ZVI-microorganisms system aids in the co-degradation of chlorinated organic compounds, enabling a high removal efficiency and adequate biological activity of the anaerobic microorganisms, to be maintained [150, 287-293]. The microbiological method may include the following processes:

a) nitrate reduction [294, 295],
b) metallic and non-metallic ion reduction [296-299],
c) phenol and its derivatives reduction [92, 300, 301],
d) removal and deactivation of viruses transferred by water [302],
e) deactivation of anaerobic Escherichia coli [303-305],
f) biosynthesis of superparamagnetic maghemite (γ-Fe$_2$O$_3$) and greigite (Fe$_3$S$_4$) nanoparticles [121, 306],
g) biosurfactant forming process, which is more effective in the presence of n-ZVI particles [307],
h) biodegradation of explosives, including 2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and hexogen (RDX) [235, 308, 309].

7. Examples of contaminant removal processes aided by n-ZVI-based composites

The following examples of contaminant removal processes using n-ZVI-based composites show excellent applicability in different processes. The key processes are:

7.1. Degradation by organic contaminant reduction

The process involves:

a) halogenated aliphatic and aromatic hydrocarbons [24, 28, 153, 274, 293, 294, 310-316],
b) azo-dyes [54, 182, 215, 317, 318],
c) pesticides [28, 103, 317, 319, 320],
d) pharmaceuticals [155, 321-325],
e) phenol derivatives [326-328],
f) thioethers [329].
7.2. Reduction/immobilization of toxic inorganic substances

Table 6 shows the reduction and sedimentation capabilities for inorganic substances, including heavy metal ions, semi-metal ions and complex non-metal ions.

Table 6. Reduction/immobilisation of inorganic contaminants using n-ZVI-based composites

| Contaminant group | Composite used with n-ZVI | Ref. |
|-------------------|---------------------------|------|
| **Heavy metal ions:** | | |
| − Cr(VI) | Fe$_3$O$_4$ | [283, 330-335] |
| | Starch | [336] |
| | Chitosan | [196, 336] |
| | − | [283, 332, 335] |
| − Hg(II) | − | [335] |
| − Pb(II) | Chitosan | [172, 234, 333, 337] |
| − Cd(II) | − | [335, 338-340] |
| − Ni(II) | − | [335, 337, 338] |
| **Semi-metal ions:** | | |
| − As(III), As(V); | Chitosan | [235, 341-348] |
| − Se(VI) | − | [235, 349, 350] |
| **Non-metallic ions:** | | |
| − ClO$_4^-$ | − | [335, 341-348] |
| − NO$_3^-$ | − | [189, 351] |
| − PO$_4^{3-}$ | Exfoliated graphite | [28, 352-357] |
| | − | [358, 359] |

7.3. High-energy material decomposition

Due to their high toxicity, all military and civil explosives and their post-detonation products are a potential hazard to human health and the environment. Explosives in production, storage and transport, due to decomposition with time or use (detonation, deflagration) are subject to dispersion, photolysis, irreversible bonding and physical sorption polluting and/or contaminating water and soil ecosystems [360-371]. Most commonly, the sources of the contamination are:

- a) explosives manufacturing plants,
- b) military bases (source of effluents containing primary explosives and their post-detonation products),
- c) storage facilities (where the withdrawn explosives may release hazardous volatile substances and may spontaneously explode),
- d) testing grounds,
- e) shooting ranges,
- f) unexploded ordnance (mostly from the 1st and 2nd World War).

Spectacular examples of environmental contamination by explosives and fissile materials are:

- a) Chesapeake Bay on the east coast of the USA, – used for over 100 years as underwater storage for toxic military materials, including ammunition [360],
- b) Semey region in the former USSR – once a nuclear weapon testing ground contaminated with radioactive materials, among them Sr$^{90}$ and referred to as nuclear waste.

A list from the US Department of Defense includes over 200 organic substances commonly used in ammunition manufacture. Table 7 shows the most commonly used toxic substances.
The effective removal of organic and inorganic contaminants using compositions...

Table 7. Selected organic substances commonly produced and used in ammunition and solid rocket fuels

| Substance | Abbreviation and common name | Chemical name | Chemical formula | Ref. |
|-----------|-----------------------------|---------------|-----------------|------|
| 2-Am-DNT  | 2-Amino-4,6-dinitrotoluene   | CH₃C₆H₄(NH₂)(NO₂)₂ |                | [43, 61, 362, 369, 372] |
| 4-Am-DNT  | 4-Amino-2,6-dinitrotoluene   |                | CH₃C₆H₄(NO₂)₂  | [43, 61, 362, 369, 373] |
| CL-20, HNIW | 2,4,6,8,10,12-Hexanitrohexaazaisowurtzitane | C₆N₁₂H₄O₁₂ |                | [43, 367, 369, 373-375] |
| DNB      | 1,3-Dinitrobenzene           | C₆H₄(NO₂)₂    |                | [43, 61, 362, 369, 372] |
| DNT      | Dinitrobenzenes: 2,4-DNT, 2,6-DNT | CH₃C₆H₄(NO₂)₂ |                | [40-43, 49, 360, 361, 366, 372, 376] |
| EGDN, glycol dinitrate | Ethyl glycol dinitrate | (CH₂ONO₂)₂ |                | [373, 375, 376] |
| GAPs     | Glycidyl azide polymer       |               |                | [40, 43, 362, 369, 373, 376] |
| HMX, octogen | 1,3,5,7-Tetranitro-1,3,5,7-tetrazoctane | C₆H₃(NO₂)₄ |                | [46, 367, 374, 375, 377] |
| NC       | Nitrocellulose               | [C₆H₉(R₂)O₅]ₙ |                | [41-43, 366, 375, 376] |
| NQ       | Nitroguanidine               | (NH₂)CN(NO₂)  |                | [42, 360, 361, 372, 376, 378] |
| NTs      | 2,3,4-Nitrotoluenes          |               |                | [43, 61, 362, 369, 375, 379] |
| PETN, penthrite | Pentaerythriol tetranitrate | C[(CH₂ONO₂)]₄ |                | [43, 362, 372, 373, 375] |
| PNCBO    | 1-Chloro-4-nitrobenzene      | ClC₆H₄NO₂     |                | [43, 269, 362, 369, 375] |
| RDX, hexogen | 1,3,5,Trinitrohexa hydro-1,3,5-triazine | C₆H₃(NO₂)₃ |                | [40, 46, 47, 61, 309, 369, 377, 380] |
| TNA      | 2,4,6-Trinitroanilin         | C₆H₃N₄O₆     |                | [362, 366, 372, 375, 376] |
| TNB      | 1,3,5-Trinitrobenzene        | C₆H₃N₄O₆     |                | [43, 61, 362, 375, 381] |
| TNG, TN  | 1,2,3-Trinitroxypropylene   | C₆H₃(NO₃)₃    |                | [43, 360, 361, 372, 375, 376] |
| TNT, trinitrotoluene | 2,4,6-Trinitrotoluene       | C₆H₃(NO₂)₃CH₃ |                | [43, 46, 50, 362, 363, 372, 375-377, 382-387] |
| Nitramine | 2,4,6-Trinitrophenyl-n-methyl nitramine | (NO₂)₃C₆H₉(N(CH₃)₃)NO₂ | | [41-43, 372, 375, 376] |

ZVI-based composites are cheap and effective agents used in the decomposition of a wide range of explosives as reported in many different studies [38-53, 60-64, 218, 235, 269, 276, 308, 309, 360-389]. The redox potential and the oxygen conditions of the soil can undergo temporal and spatial changes thereby determining both the mechanism and the rate of their decomposition. Other key parameters are the moisture content and the microbiological activity of the edaphon (bacteria, earthworms and other invertebrates) [21-26]. In typical conventional explosives, including TNT, RDX, HMX, the former affects the biodegradation rate of other materials [390]. Adding 1 wt.% of Cl⁻ or Br⁻ ions to the mixture results in a significant increase in both efficiency and rate of their degradation [39].

Another list from the US Department of Defence includes inorganic substances [391-400]:

a) ammonium, potassium and lithium perchlorates;
b) ammonium, potassium and sodium nitrates;
c) alloys: Al-Mg, Zn, Ti, Mo, Cr, Zn,
d) metals: Be, Cu, Fe, Pb, Zn,
e) non-metals: S, P (white), P (yellow), B, Si,
f) oxides: BaO₂, PbO₂, Pb₃O₄,
g) inorganic compounds: mercury(II) fulminate Hg(CNO)₂, lead(II) azide Pb(N₃)₂.
Also, a number of monitored toxic organometallic compounds are commonly used, including:

- tetraethyl lead, Pb(C₂H₅)₄,
- mesoporous chelate polymers, e.g. MOF-Fe-ML-101-NH₂,
- carbon composites and organometallic compounds used as carriers.

### 7.4. Radioactive material (nuclear waste) deactivation

It has been shown that n-ZVI particles are also effective in the removal of radioactive elements from groundwater using PRBs [401-403] as well as their reduction by the injection of a colloidal aqueous suspension of n-ZVI particles into the contaminant’s flow [404]. In practice, the n-ZVI based composites are used to remove U(VI) ions in:

- mine effluents [63, 405],
- contaminated water environment (groundwater) [406-409],
- treated water [410-412].

### 7.5. Field applications

Most field applications utilize the reducing properties of primary ZVI particles coated with suitable agents which reduce their aggregation and sedimentation properties and stabilize their activity [1, 2, 8, 9, 18, 21-26, 404]. A significant increase in the effectiveness of ZVI-based composites has been achieved by doping the primary ZVI particles with other metals [27, 34, 133, 178, 259].

In the environment being remediated, the nanoparticles are distributed using different liquid, the most common being water, nitrogen, vegetable oils or suitable water and oil mixtures. The liquid preparations are usually introduced into the remediation area every 10 m [21-25, 413].

From the point of view of the in-situ practical field applications of engineered nanoparticles in the environmental remediation process, the particles should show the following properties:

- high efficiency in contaminant reduction [21-27, 35, 57, 59, 103, 216, 257]. The results of field tests have shown significant differences in the effectiveness of ZVI particles in the mm-, μm- and nanoscale [6, 178],
- good mobility in a porous medium [21, 97, 103, 162, 178, 247, 248, 413],
- sufficient effective time of action (stability) [28, 57, 89, 176, 178, 187],
- low toxicity [20-24, 35, 103, 414].

An example of a chemical composition of the reducing mixture used in practice [21, 25, 413, 414] is:

- concentrated aqueous n-ZVI suspension (20-30 nm, 255 g/dm³),
- emulsifier (6 g/dm³ xanthan gum biopolymer),
- 43% H₂O₂,
- 37.2% vegetable oil,
- 1.5% SPC (surfactant).

A key issue limiting the practical application of n-ZVI particles in soil and water ecosystem remediation processes, is their high susceptibility to aggregation, resulting in limited mobility [57, 89, 176, 187].

### 8. Concerns related to the environmental release of n-ZVI particles

The constantly growing number of practical applications of highly-dispersed ZVI particles is inextricably linked with concerns related to an inadequate knowledge of their ecotoxicity. Published studies have shown that the current knowledge of concentration, latency time, environmental fate, mobility and ecotoxicity of the n-ZVI particles is evaluated critically. It is recommended that, to promote innovative ecological methods of nanoparticle synthesis and the introduction of international legislation, would require the monitoring of all types of nanoparticles released into the environment. The issue of n-ZVI ecotoxicity cannot be underestimated considering the mistakes made in common applications of ACMs [415], PCBs [416], polychlorinated terphenyls (PCTs) [417], CFCs and HCFCs [418, 419].
Test results for the mechanism of n-ZVI interaction with living organisms, suggest that its toxicity can be caused by:

a) direct interaction with the biological components of the organism,
b) oxidative stress of the compounds generated by the n-ZVI in aqueous phase,
c) release of Fe(II) and Fe(III) ions by the primary n-ZVI particles used in the Fenton reaction [264, 280].

The majority of studies focused on the toxicity of n-ZVI particles on microorganisms. Many reported that the particles are toxic to some bacteria, including Pseudomonas stutzeri and Escherichia coli [305, 420-422]. A specific mode of action of n-ZVI particles involves causing oxidative stress by the release of reactive oxygen-containing chemical species, i.e. ROS formed in the Fenton reaction [264, 280]. In general, the interaction of n-ZVI particles with microorganisms is highly diverse, depending on the type, physical and chemical properties of the nanoparticle coating and the medium [420, 423].

In the case of aquatic organisms, the possibility of contact with n-ZVI particles is limited to the body of water or remediation area. The results of studies have shown that n-ZVI particles and their oxidation products are toxic to fresh and saltwater organisms (phytoplankton, plankton – Daphnia magna, water flea), spawn and fish in their early stages of development (Orgias lapites – Japanese rice fish) [424-426]. A high diversity of negative effects were observed in marine microalgae cultures [244, 426]. Studies on the effects of n-ZVI particles on land organisms are sparse and do not include remediation areas where those particles were used. Special attention was paid to organisms present in the soil, known as the edaphon (bacteria, earthworms and other invertebrates). Results of these studies showed the adverse effects of n-ZVI particles on soil, resulting in changes in earthworm (Eisenia fetida and Lumbricus rubellus) body mass and mortality rate at particle concentrations over 500 mg/g [320, 427-429]. The effects of n-ZVI particles on plants, referred to in some studies, involve phytotoxicity and possible bioaccumulation [420-422, 430-432].

9. Summary

Analysis of studies dealing with aspects of n-ZVI particles led to the following conclusions:

♦) Replacing ZVI particles in at macro and micro scale with nanoparticles, n-ZVI allows the contaminant reduction processes to be carried out while increasing its effectiveness as a reducing agent and a catalyst for decomposition of both organic and inorganic hazardous substances.

♦) Recent developments in n-ZVI particle synthesis have led to limiting the use of hazardous reducing agents.

♦) The high susceptibility of ZVI nanoparticles to aggregation and settling is a key issue in the practical applications of remediation to water and soil ecosystems, sediments and waste recycling sites.

♦) Surface modification of the primary n-ZVI particles with coatings, mixtures or doping with other metals, significantly improves their stability and effectiveness. The chemical composition of the n-ZVI surface significantly affects its mobility and depends on the modifying agent used and extant geochemical conditions.

♦) New and innovative solutions in environmental protection (E-Nano), may bring benefits but may also have negative effects. The following integrated, preventive approach is proposed to mitigate the issue:

– innovative and eco-friendly methods of synthesising primary nanoparticles and n-ZVI-based composites,
– monitoring of nanoparticles released into the environment,
– national and international legislation on nanoparticles,
– intensification and consolidation of research into the effects of n-ZVI on humans, fauna and flora.

♦) The observed results generally show that ZVI nanoparticles are harmless to the environment and are converted into naturally occurring oxides. Some reports suggest that some nanoparticles may permeate cell membranes and the blood-brain barrier. Nanoparticles showing high chemical reactivity, when inhaled, may have adverse future effects which are difficult to predict.
References

[1] a) Foltynowicz Z., Czajka B., Maranda A., Wachowski L. Aspects of Nanomaterials for Civil and Military Applications Part 1. The Origin, Characterization and Methods of Obtaining. (in Polish) *Mater. Wysokoenerg.* 2017, 9: 5-17; b) English version in this issue: *Mater. Wysokoenerg. (High Energy Mater.)* 2020, 12(1): 5-16.

[2] a) Foltynowicz Z., Czajka B., Maranda A., Wachowski L. Aspects of Nanomaterials for Civil and Military Applications. Part 2. The Use of and Concerns Arising from Infiltration of the Natural Environment. (in Polish) *Mater. Wysokoenerg.* 2017, 9: 18-39; b) English version in this issue: *Mater. Wysokoenerg. (High Energy Mater.)* 2020, 12(1): 17-36.

[3] a) Czajka B., Sałaciński T., Wachowski L., Maranda A. High-Energy Materials (HEMs) – Innovations with Regard to the Environment. (in Polish) *Mater. Wysokoenerg.* 2017, 9: 40-55; b) English version in this issue: *Mater. Wysokoenerg. (High Energy Mater.)* 2020, 12(1): 75-89.

[4] Roehl K.E., Huttenloch P., Czurda K. Permeable Sorption Barriers for in-situ Remediation of Polluted Groundwater – Reactive Materials and Reaction Mechanisms. [in:] *Green 3, The Exploitation of Natural Resources and the Consequences.* London: Thomas Telford Publishing, 2001, pp. 466-473.

[5] Moraci N., Calabro P.S. Heavy Metals Removal and Hydraulic Performance in Zero-Valent Iron/Pumice Permeable Reactive Barriers. *J. Environ. Manag.* 2010, 91: 2336-2341.

[6] Comba S., Molfetta D.A., Sethi R. A Comparison between Feld Applications of Nano-, Micro-, and Millimetric Zero-Valent Iron for the Remediation of Contaminated Aquifers. *Water Air Soil Pollut.* 2011, 215: 595-607.

[7] Moraci N., Ielo D., Bilardi S., Calabro P.S. Modelling Long Term Hydraulic Conductivity Behaviour of Zero Valent Iron Column Tests for PRB’s Design. *Can. Geotech. J.* 2016, 53: 946-961.

[8] Obiri-Nyarko F., Grajales-Mesa J., Malina G. An Overview of Permeable Reactive Barriers for in-situ Sustainable Groundwater Remediation. *Chemosphere* 2014, 111: 243-259.

[9] Gavaskar A., Gupta N., Sass B., Janosy R., Hicks J. Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation. *J. Environ. Manag.* 2010, 91: 2336-2341.

[10] Pawluk K., Lendo-Siwicka M., Wrzesiński G. Technologies for Permeable Reactive Barriers. (in Polish) *Acta Sci. Pol. Architectura* 2017, 16(2): 91-99.

[11] Li L., Benson C.H., Lawson E.M. Modelling Porosity Reductions Caused by Mineral Fouling in Continuous-wall Permeable Reactive Barriers. *J. Contam. Hydrol.* 2006, 83: 89-121.

[12] Pawluk K. Mechanical Properties of Selected Reactive Materials. (in Polish) *Acta Sci. Pol. Architectura* 2015, 14(3): 57-66.

[13] Pawluk K., Fronczyk J. Evaluation of Single and Multilayered Reactive Zones for Heavy Metals Removal from Stormwater. *Environ. Technol.* 2015, 36(12): 1576-1583.

[14] Pawluk K., Fronczyk J., Garbulewski K. Reactivity of Nano Zero-valent Iron in Permeable Reactive Barriers. *Pol. J. Chem. Technol.* 2015, 17(1): 7-10.

[15] Noubactep C. On the Operating Mode of Bimetallic Systems for Environmental Remediation. *J. Hazard. Mater.* 2009, 164: 394-395.

[16] Noubactep C., Meinrath G., Dietrich P., Sauter M., Merkel B. Testing the Suitability of Zerovalement Iron Materials for Reactive Walls. *Environ. Chem.* 2005, 2: 71-76.

[17] Naidu R., Birke V. *Permeable Reactive Barrier Sustainable Groundwater Remediation.* Boca Raton: CRC Press, 2014.

[18] Theodore L., Kunz R. *Nanotechnology: Environmental Applications and Solutions.* Hoboken/New York: J. Willey, 2005.

[19] Noubactep C. An Analysis of the Evolution of Reactive Species in Fe/H2O Systems. *J. Hazard. Mater.* 2009, 168: 1626-1631.

[20] Bystrzejewska-Piotrowska G., Golimowski J., Urban P.L. Nanoparticles: Their Potential Toxicity, Waste and Environment and Management. *Waste Manage.* 2009, 29: 2587-2595.
The effective removal of organic and inorganic contaminants using compositions...

[21] Crane R.A., Scott T.B. Nanoscale Zero-Valent Iron: Future Prospects for an Emerging. J. Hazard. Mater. 2012, 211-212; 112-125.
[22] Tratnyek P.G., Johnson R.L. Nanotechnologies for Environmental Clean up. Nano Today 2006, 1: 44-48.
[23] Noubactep C. Metallic Iron for Environmental Remediation: A Review of Reviews. Water Res. 2015, 45: 114-123.
[24] Fu F., Dionysiou D.D., Liu H. The Use of Zero-Valent Iron for Groundwater Remediation and Waste Water Treatment: A Review. J. Hazard. Mater. 2014, 267: 194-205.
[25] Jortner J., Rao C.N. Nanostructured Advanced Materials. Perspectives and Directions. Pure Appl. Chem. 2002, 74: 1491-1506.
[26] Phillips D.H., Van Nooten T., Bastiaens L., Russell M.I., Dickson K., Plant S., Ahad J.M.E., Newton T., Elliot T., Kalin R.M. Ten Year Performance Evaluation of a Field-scale Zero-Valent Iron Permeable Reactive Barrier Installed to RemEDIATE Trichloroethene Contaminated Groundwater. Environ. Sci. Technol. 2010, 44: 3861-3869.
[27] O’Carroll D., Sleep B., Krol M., Boparai H., Kocur C. Nanoscale Zero Valent Iron and Bimetallic Particles for Contaminated Site Remediation. Adv. Water Resour. 2013, 51: 104-122.
[28] Zhang W.X. Nanoscale Iron Particles for Environmental Remediation: An Overview. J. Nanopart. Res. 2003, 5: 323-332.
[29] Xing L., Brink G.H., Chen B., Hofer F., Kooi B.J., PalasAntzas G. Synthesis and Morphology Iron-Iron Oxide Core-Shell Nanoparticles Produced by High Pressure Gas Concentration. Nanotechnology 2016, 27(21): 215703.
[30] Hwang Y.-H., Shin H.-S. Effects on Nano Zero-Valent Iron Reactivity of Interactions between Hardness, Alkalinity, and Natural Organic Matter in Reverse Osmosis Concentrate. J. Environ. Sci. 2013, 25: 2177-2184.
[31] Hwang Y.H., Kim D.G., Shin H.-S. Effects of Synthesis Conditions on the Characteristics and Reactivity of Nano Scale Zero Valent Iron. Appl. Catal. B: Environ. 2011, 105: 144-150.
[32] Mueller N.C., Braun J., Bruns J., Černík M., Rissing P., Rickerby D. Application of Nanoscale Zero Valent Iron (NZVI) for Groundwater Remediation in Europe. Environ. Sci. Pollut. Res. Int. 2012, 9(2): 550-558.
[33] Shih Y.H., Hsu C.Y., Su Y.F. Reduction of Hexachlorobenzene by Nanoscale Zerovalent Iron: Kinetics, pH Effect, and Degradation Mechanism. Separ. Purif. Technol. 2011, 76: 268-274.
[34] Lien L., Elliott D.W., Sun Y.P., Zhang W.X. Recent Progress in Zerovalent Iron Nanoparticles for Groundwater Remediation. J. Environ. Eng. Manage. 2006, 16(6): 371-380.
[35] Mukherjee R., Kumar R., Sinha A., Lama Y., Saha A.K. A Review on Synthesis, Characterisation and Applications of Nano Zero Valen t Iron (nZVI) for Environmental Remediation. Crit. Rev.Environ. Sci. Technol. 2016, 46(5): 443-466.
[36] Li X.Q., Elliott D.W., Zhang W. Zero Valen t Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering Aspects. Crit. Rev. Solid State Mater. Sci. 2006, 31: 111-122.
[37] Selvaran M., Prema P. Removal of Toxic Metal Hexavalent Chromium[Cr(VI)] from Aqueous Solution Using Starch-stabilized Nanoscale Zerovalent Iron as Adsorbent: Equilibrium and Kinetics. Int. J. Environ. Sci. 2012, 2: 1962-1975.
[38] Brannon M., Myers T.E. Review of Fate and Transport Processes of Explosives. U.S. Army Corps of Engineers, Technical Report IRRP-97-2, US, 1997.
[39] Kim J.S., Shea P.J., Yang J.E., Kim J.E. Halide Salts Accelerate Degradation of High Explosives by Zero-valent Iron. Environ. Pollut. 2007, 147: 634-641.
[40] Glovere D.J., Hoffsommer J.C. Photolysis of RDX: Identification and Reaction Products. Naval Surface Weapons Center, Technical Report NSWCTR-79-349, Silver Spring (MD), 1979.
[41] McGrath C.J. Review of Formulations for Processes Affecting the Subsurface Transport of Explosives. U.S. Army Corps of Engineers, Technical Report IRRP-95-2, Waterways Experiment Station, 1995.
[42] Rosenblatt D.H., Burrows E.P., Mitchell W.R., Palmer D.L. Organic Explosives and Related Compounds.
[in:] The Handbook of Environmental Chemistry. Hutzinger O. Ed., Berlin: Springer, 1989, Vol. 3, pp. 195-234.

[43] Karnjanapiboonwong A., Zhang B., Freitag C.M., Dobrovolny M., Salice C.J., Smith P.N., Kendall R.J., Anderson T.A. Reproductive Toxicity of Nitroaromatics to the Cricket, Acheta domesticus. Sci. Total Environ. 2009, 407(18): 5046-5049.

[44] Hampton M.L., Sisk W.E. Environmental Stability of Windrow Composting of Explosives Contaminated Soils. [in:] Emerging Technologies in Hazardous Waste Management IX. Tedder D.W. Ed., Washington: Division of Industrial and Engineering Chemistry, A Sm. Chem. Soc., 1997, 252-257.

[45] Toxicity of Marine Sediments and Pore Waters Spiked with Ordnance Compounds. NFESC, Report Number CR 01-001-ENV, Naval Facilities Engineering Command, 2000.

[46] Lynch J.C. Dissolution Kinetics of High Explosive Compounds (TNT, RDX, HMX). U.S. Army Engineering Research and Development, ERDC/EL TR-02-23, 2002.

[47] Naja G., Halasz A., Thiboutot S., Ampleman G., Havari J. Degradation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) using Zerovalent Nanoparticles. Environ. Sci. Technol. 2008, 42(12): 4364-4370.

[48] Saad R., Thiboutot S., Ampleman G., Dashan W., Hawari J. Degradation of Yrinitroglycerin (TNG) using Zero-Valent Iron Nanoparticles/Nanosilica SBA-15 Composite (ZVINs/SBA-15). Chemosphere 2010, 81: 853-858.

[49] Akhavan J. The Chemistry of Explosives. 2nd ed., RSC Paperbacks, Cambridge: Royal Society of Chemistry, 2004.

[50] Zhao Q., Ye Z., Wang Z., Zhang M. Progress on the Treatment of TNT Waste Water. Environ. Chem. 2010, 29(5): 496-801.

[51] Sittig M. Handbook of Toxicant Hazardous Chemicals. 3rd ed., Park Ridge (NJ): Noyes Pub, 1991.

[52] Brannon J.M., Pennington J.C. Environmental Fate and Transport Process Descriptors for Explosives. U.S. Army Engineer Research and Development Center, ERDC/ELTR-02-10, 2002.

[53] Hennecke D., Kordel W., Steinbach K., Herrmann B. Transformation Processes of Explosives in Natural Water/Sediment Systems. Proc. 10th Int. UFZ Deltas/TNO Conf. on Management of Soil, Groundwater and Sediments, Milano, Italy, 2008.

[54] Satapanajaru T., Chompuchan C., Suntornchot P., Pengthamkeerati P. Enhancing Decolorization of Reactive Black 5 and Reactive Red 198 during Nano Zerovalent Iron Treatment. Desalination 2011, 266: 218-230.

[55] Wen Z., Zhang Y., Dai C. Removal of Phosphate from Aqueous Solution Using Nanoscale Zerovalent Iron (nZVI). Colloids Surf., A 2014, 457: 433-440.

[56] Wu D., Shen Y., Ding A., Qiu M., Yang Q., Zheng S. Phosphate Removal from Aqueous Solutions by Nanoscale Zero-Valent Iron. Environ. Technol. 2013, 34: 2663-2669.

[57] Allabaksh M.B., Mandal B.K., Kesarla M.K., Kumar K.S., Pamanji S.R. Preparation of Stable Zero Valent Iron Nanoparticles Using Different Chelating Agents. J. Chem. Pharm. Res. 2010, 2(5): 67-74.

[58] Hawari J. Biodegradation of RDX and HMX: from Basic Research to Field Application. [in:] Biodegradation of Nitroaromatic Compounds and Explosives. Spain J.C., Hughes J.B., Knackmuss H.J. Eds., Boca Raton: CRC Press, 2000, 277-310.

[59] Zhao J.S., Fournier D., Thiboutot S., Ampleman G., Hawari J. Biodegradation and Bioremediation of Explosives. [in:] Applied Bioremediation and Phytoremediation. Singh A., Ward O.P. Eds., Heidelberg/Berlin: Springer Verlag, 2004, 55-80.

[60] Jones A.M., Greer C.W., Ampleman G., Thiboutot S., Lavigne J., Hawari J. Biodegradability of Higher Energetic Chemicals under Aerobic Conditions. Proc. 3rd Int. Conf. on in situ and on site Bioreclamation, San Diego, CA, 1995.

[61] Huang Q., Shi X., Pinto R.A., Petersen E.J., Weber Jr. W.J. Tunable Synthesis and Immobilization of Zero-Valent Iron Nanoparticles for Environmental Applications. Environ. Sci. Technol. 2008, 42(23): 8884-8889.

[62] U.S. Army Corps of Engineers. Distribution and Fate of Energetic on DoD Test and Training Ranges.
Strategic Environment Research and Development Program, Final Report ERDC-TR-06-13, 2006.

[63] Dickinson M., Scott T.B. The Application of Zero-Valent Iron Nanoparticles for the Remediation of a Uranium-contaminated Waste Effluent. *J. Hazard. Mater.* 2010, 178: 171-179.

[64] Liang L., Gu B., Yin X. Removal of Technetium-99 from Contaminated Groundwater with Sorbents and Reductive Materials. *Sep. Technol.* 1996, 6: 111-122.

[65] Milkovič O., Janák G., Nižník Š., Longauer S., Fröhlich L. Iron Nanoparticles Produced by Precipitation Phenomena in Solid State. *Mater. Lett.* 2010, 64: 144-146.

[66] Han Y., Yang M.D.Y., Zhang W. Optimizing Synthesis Conditions of Nanoscale Zero-Valent Iron (nZVI) through Aqueous Reactivity Assessment. *Frontiers Environ. Sci. Eng.* 2015, 9(5): 813-822.

[67] Ghauch A. Iron-based Metallic Systems: An Excellent Choice for Sustainable Water Treatment. *Freib. Online Geo sci.* 2015, 38: 1-80.

[68] Cheong S., Ferguson P., Feindel K.W., Devonshire E. The Purification of Water by Means of Metallic Iron. *J. Frankl. Inst.* 1890, 129: 449-461.

[69] Baylis J.R. Prevention of Corrosion and “Red Water”. *J. Am. Water Works Assoc.* 1926, 15: 598-633.

[70] Baker M. Sketch of the History of Water Treatment. *J. Am. Water Works Assoc.* 1934, 269: 902-938.

[71] Ling L., Zhang W.-X. Sequestration of Arsenate in Zero-Valent Iron Nanoparticles: Visualisation of Intraparticle Reactions at Angstrom Resolutions. *Environ. Sci. Technol.* 2014, 3(12): 305-309.

[72] Bischof G. On Putrescent Organic Matter in Potable Water. I. *Proc. R. Soc. London* 1877, 26: 179-184.

[73] Bischof G. On Putrescent Organic Matter in Potable Water. II. *Proc R. Soc. London* 1878, 27: 258-261.

[74] Miyajima K., Noubactep C. Characterizing the Impact of Sand Addition on the Efficiency of Granular Iron for Water Treatment. *Chem. Eng. J.* 2015, 262: 891-896.

[75] Li S., Ding Y., Wang W., Lei H. A Facile Method for Determining the Fe(0) Content and Reactivity of Zero Valent Iron. *Anal. Methods* 2016, 8: 1239-1298.

[76] Miyajima K., Noubactep C. Effects of Mixing Granular Iron with Sand on the Efficiency of Methylene Blue Discoloration. *Chem. Eng. J.* 2012, 200: 33-438.

[77] Attia A.A., Girgis B.S., Fathy N.A. Removal of Methylene Blue Discoloration. *Chem. Eng. J.* 2016, 287: 618-632.

[78] Miyajima K. Optimizing the Design of Metallic Iron Filters for Water Treatment. *Freib Online Geo sci.* 2012, 32: 60.

[79] Arnold W.A., Roberts A.L. Pathways and Kinetics of Chlorinated Ethylene and Chlorinated Acetylene Reaction with Fe\(^{0}\) Particles. *Environ. Sci. Technol.* 2000, 34: 1794-1805.

[80] Lien H.L., Zhang W.-x. Nanoscale Iron Particles for Complete Reduction of Chlorinated Ethenes. *Colloids Surf. A: Physicocem. Eng. Aspects* 2001, 191(1-2): 97-105.

[81] Zhang X.W., Elliott D.W. Applications of Iron Nanoparticles for Groundwater Remediation. *Remediation* 2006, 16: 7-21.

[82] Ahmadi M., Mashhon F., Kaveh R., Tarkian F. Use of Mechanically Prepared Iron Nanoparticles for Nitrate Removal from Water. *Asian J. Chem.* 2011, 23(3): 1205-1208.

[83] Bigg T., Judd S.J. Zero-Valent Iron for Water Treatment. *Environ. Technol.* 2000, 21: 661-670.

[84] Chen L., Jin S., Faigren P.H., Swoboda-Colberg N.G., Liu F., Colberg P.J.S. Electrochemical Depassivation of Zero-Valent Iron for Trichloroethene Reduction. *J. Hazard. Mater.* 2012, 239-240: 265-269.
Supported Nano Zero-Valent Iron (nZVI) Particles with Enhanced Stability and Activity for Hexavalent Chromium Reduction. *J. Hazardous Mater.* 2016, 309: 249-258.

[90] Iravani S. Green Synthesis of Metal Nanoparticles Using Plants. *Green Chem.* 2011, 13(10): 2638-2650.

[91] Amouzadeh M.T., Tvakkoli V., Dhand K., Rhee K.Y., Park J. Eco-friendly One Pot Synthesis of Gold Decorated Reduced Grapheme Oxide Using Beer as Reducing Agent. *J. Indust. Eng. Chem.* 2014, 20(4): 4327-4331.

[92] Yan W., Lien H.L., Koel B.E., Zhang W.X. Iron Nanoparticles for Environmental Clean-Up: Recent Developments and Future Outlook. *Environ. Sci. Process Impacts* 2013, 15(1): 63-77.

[93] Deng Z., Zhang K.C., Chan L., Liu T.L. Fe-based Metallic Glass Catalyst with Nanoporous Surface for Azo Dye Degradation. *Chemosphere* 2017, 174: 76-81.

[94] Sun Y.P., Li X.Q., Cao J., Zhang W.X., Wang H.P. Characterization of Zero-Valent Nanoparticles. *Adv. Colloid Interface Sci.* 2006, 120: 47-56.

[95] Liu H.B., Chen T.H., Chang D.Y., Chen D., Liu Y., He H.P., Yuan P., Frost R. Nitrate Reduction over Nanoscale Zero-Valent Iron Prepared by Hydrogen Reduction of Goethite. *Mater. Chem. Phys.* 2012, 133: 205-211.

[96] Kahoul A., Hammouche A. Electrochemical Performances of FePO$_4$ – Positive Mass Prepared through a New Sol-gel Method. *Ionics* 2010, 16(2): 105-109.

[97] Chandraekaran P., Viruthagiri G., Srinivasam N. The Effect of Various Capping Agents on the Surface Modifications of Sol-Gel Synthesised ZnO Nanoparticles. *J. Alloy Compd.* 2012, 540: 47-56.

[98] Wright J.S., Sommerdijk N.A.J.M. *Sol-gel Methods: Chemistry and Applications.* CRC Press, 2000.

[99] Chin S.A.B., Yaacob I.I. Synthesis and Characterization of Magnetic Iron Nanoparticle via W/O Microemulsion and Massat’s Procedure. *J. Mater. Process. Technol.* 2007, 191(1-3): 235-237.

[100] Li L., Fan M., Brown R.C., Van Leeuwen J.H., Wang J., Wang W., Sang Y., Zhang P. Synthesis, Properties and Environmental Applications of Nanoscale Iron-based Materials: A Review. *Crit. Rev. Environ. Sci. Technol.* 2006, 36(5): 405-431.

[101] Balco B.A., Tratnyek P.G. Photoeffects on the Reduction of Carbon Tetrachloride by Zero-Valent Iron. *J. Phys. Chem. B* 1995, 102(8): 1459-1465.

[102] Nam S., Tratnyek P.G. Reduction of Azo-dyes by Zero-Valent Iron. *Water Res.* 2000, 34: 837-845.

[103] *Aquatic Redox Chemistry.* Tratnyek P.G., Grundl T.J., Haderlein S.B. Eds., Am. Chem. Soc. Ser., ACS Symp. Ser., Washington (D.C.), 2011, Vol. 1071.

[104] Matos J., Rosesales M., Garcia A., Nieto-Delgado C., Rangel-Mendez J.R. Hybrid Photoactive Materials from Municipal Sewage Sludge for the Photocatalytic Degradation of Methylene Blue. *Green Chem.* 2011, 13(12): 3431-3439.

[105] Chia H.-C., Yeh C.-S. Hydrothermal Synthesis of SnO$_2$ Nanoparticles and Their Gas Sensor of Alcohol. *J. Phys. Chem. C* 2007, 111: 7256-7259.

[106] Zbořil R., Mashlan M., Petridis D. Iron(III) Oxides from Thermal Processes Synthesis, Structural and Magnetic Properties, Mössbauer Spectroscopy Characterization, and Applications. *Chem. Mater.* 2002, 14: 969-982.

[107] Noubactep C., Care S. On Nanoscale Metallic Iron for Groundwater Remediation. *J. Hazard. Mater.* 2010, 182: 923-927.

[108] Chowdhury P.S., Arya P.R., Raha K. Green Synthesis of Nanoscopic Iron Oxide Particles: A Potential Oxidizer in Nanoenergetics. *Synth. React. Inorg. Met.-Org. Chem.* 2007, 37(6): 447-451.

[109] Genuino H.C., Huang H., Njagi E.C., Stafford L., Suib S.L. *A Review of Green Synthesis of Nanophase Inorganic Materials for Green Chemistry Applications.* Handbook of Green Chemistry. J. Willey-VCH, 2012.

[110] Gao S., Shi Y., Zhang S., Jiang K., Yang S., Li Z.E. Takayama-Muromachi, Biopolymer-assisted Green Synthesis Iron Oxide Nanoparticles and Their Magnetic Properties. *J. Phys. Chem. C* 2008, 112(28):
The effective removal of organic and inorganic contaminants using compositions...

10398-10401.

[111] Meeks N.D., Smuleac V., Stevens C., Bhattacharyya D. Iron-based Nanoparticles for Toxic Organic Degradation: Silica Platform and Green Synthesis. *Ind. Eng. Chem. Res.* 2012, 51(28): 9581-9590.

[112] Smuleac V., Varma R., Sikdar S., Bhattaryya D. Green Synthesis of Fe and Fe/Pd Bimetallic Nanoparticles in Membranes for Reductive Degradation of Chlorinated Organics. *J. Membrane Sci.* 2011, 379(1-2): 131-137.

[113] Aranz S., Chiva-Blanch G., Valderas-Martinez P., Medina-Remón A., Lamuela-Raventós R.M., Estruch R. Wine, Beer, Alcohol and Poliphenols and Cardiovascular Disease and Cancer. *Nutrients* 2012, 4: 759-781.

[114] Nadagouda M.N., Hoag G., Collins R.S., Varma R.S. Green Synthesis of Au Nanostructures at Room Temperature Using Biodegradable Plant Surfactants. *Cryst. Growth Des.* 2009, 9(11): 4979-4983.

[115] Manquín-Cerda K., Cruces E., Rubio A.M., Reyes C., Arancibia-Miranda N. Preparation of Nanoscale Iron (Oxide, Oxyhydroxides and Zero-Valent) Particles Derived from Blueberries: Reactivity, Characterization and Removal Mechanism of Arsenate. *Ecotoxicol. Environ. Safety* 2017, 145: 69-77.

[116] Hoag G.E., Collins J.B., Holcomb J.L., Hoag J.R., Nadagouda M.N., Vanna R.S. Degradation of Bromothymol Blue by “Greener” Nano-scale Zero-Valent Iron Synthesized Using Tea Polyphenols. *J. Mater. Chem.* 2009, 19(45): 8671-8677.

[117] Sharma R.K., Gulati S., Mehta S. Preparation of Gold Nanoparticles Using Tea: a Green Chemistry Experiment. *J. Chem. Educ.* 2012, 89(10): 1326-1318.

[118] Aromal S.A., Philip D. Green Synthesis of Gold Nanoparticles Using Trigonella Foenum-graecum and Its Size-dependent Catalytic Activity. *Spectrochim. Acta Part A. Mol. Bipomol. Spectrosc.* 2012, 97: 1-5.

[119] Njagi E.C., Huang H., Stafford L., Genuino H., Galindo H.M., Collions J.B., Hoag G.E., Nadagouda M.N., Vanna R.S. Green Synthesis of Au Nanostructures at Room Temperature Using Aqueous Sorghum Bran Extracts. *Langmuir* 2011, 27(1): 264-271.

[120] Lovley D.R., Stoltz J.F., Nord Jr. G.L., Phillips E.J.P. Anaerobic Production of Magnetite by Dissimilatory Iron-reducing Microorganism. *Nature* 1987, 330(6145): 252-254.

[121] Bhardre A.A., Parikh R.Y., Baidakova M., Jouen S., Hannoyer B., Enoki T., Prasad B.L.V., Shouche Y.S., Ogale S., Sastry M. Bacterial-mediated Precursor-dependent Biosynthesis of Superparamagnetic Iron Oxide and Iron Sulphide Nanoparticles. *Langmuir* 2008, 24(1): 5787-5794.

[122] Dhillon G.S., Brar S.K., Kaur S., Verma M. Green Approach for Nanoparticle Biosynthesis by Fungi Current Trends and Applications. *Crit. Rev. Biotechnol.* 2012, 32(1): 49-73.

[123] Bhardre A., Wani A., Shouche Y., Joy P.A., Prasad B.L.V., Sastry M. Bacterial Aerobic Synthesis of Nanocrystalline Magnetite. *J. Am. Chem. Soc.* 2005, 127(6): 9326-9327.

[124] Vigneshwaran N., Ashapatire N.M., Varadarajan P.V., Nachane R.P., Paralikar K.M., Balasubramanya R.H. Biological Synthesis of Silver Nanoparticles Using the fungus Aspergillus flavus. *Mater. Lett.* 2007, 61(6): 1413-1418.

[125] Bhaede A., Rautaray D., Bansal V., Ahmad A., Sarkar I., Yusuf S.M., Sanyal M., Sastry M. Extracellular Biosynthesis of Magnetite Using Fungi. *Small* 2006, 2(1): 135-141.

[126] Lee C.-L., Jou C.-J.G. Reduced Degradation of Chlorobenzene in Cosolvent Solution Using Nanoscale Zero-Valent Iron with Microwave Irradiation. *Environ. Eng. Sci.* 2011, 28(3):191-195.

[127] Vitta Y., Piscitelli V., Fernandez A., Gonzalez-Jimenez F., Castillo J. α-Fe Nanoparticles Produced by Laser Ablation: Optical and Magnetic Properties. *Chem. Phys. Lett.* 2011, 512: 96-98.

[128] Kassae M.Z., Motamed E., Mikhak A., Rahnemaie R. Nitrate Removal from Water Using Iron Nanoparticles Produced by Arc Discharge vs. Reduction. *Chem. Eng. J.* 2011, 166: 490-495.

[129] Eljamal R., Eljamal O., Khalil A.M.E., Saha B.B., Matsunaya N. Improvement of the Chemical Synthesis Efficiency of Nanoscale Zero-Valent Iron Particles. *J. Environ. Chem. Eng.* 2018, 6(4): 4727-4735.

[130] Nurmi J.T., Tratnyek P.G., Sarathy V., Baer D.R., Amonette J.E., Pecher K., Wang Ch., Linehan J.C., Matson D.W., Penn R.L., Driessen M.D. Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry, and Kinetics. *Environ. Sci. Technol.* 2005, 39(5): 1221-1230.

[131] Laumann S., Micić V., Hofmann T. Mobility Enhancement of Nanoscale Zero-Valent Iron in Carbonate
Porous Media through co-Injection of Polyelectrolytes. *Water Res.* **2014**, *250*: 70-79.

[132] Karri S., Sierra-Alvarez R., Field J.A. Zero Valent Iron as an Electron-donor for Methanogenesis and Sulfate Reduction in Anaerobic Sludge. *Biotechnol. Bioengin.* **2005**, *92*(7): 810-819.

[133] Liou Y.H., Lo S., Kuan W.H., Lin C., Weng S.C. Effect of Precursor Concentration on the Characteristics of Nanoscale Zerovalent Iron and Its Reactivity of Nitrate. *Water Res.*** **2006**, *40*: 2485-2492.

[134] Yaron-Marcovich D., Chen Y., Nir S., Prost R. High Resolution Electron Microscopy Stimulated Studies of Organo-clay Nanoparticles. *Environ. Sci. Technol.* **2005**, *39*(5): 1231-1238.

[135] Herrera-Becerra R., Zorrilla C., Rius J.L., Ascencio J.A. Electron Microscopy Characterization of Bio-synthesized Iron Oxide Nanoparticles. *Appl. Phys. Process.* **2008**, *91*(2): 241-246.

[136] Wang C.M., Baer D.R., Engelhard M.H., Amonette J.E., Antony J.J., Qiang Y. Fine Structural Features and Electronic Structure of Core-Shell Structured Fe Nanoparticles Probed Using TEM/STEM and EELS. *Microsc. Microanal.* **2009**, *15*: 1204-1205.

[137] Yamamoto H., Morley M.C., Speitel G.E., Clausen J. Fate and Transport of High Explosives in a Sandy Soil: Adsorption and Desorption. *Soil Sediment Contam.* **2004**, *13*(5): 459-477.

[138] Gabbasov R., Polikarpov M., Cherepanov V., Chuev M., Mischenko I., Lomov A., Wang A., Panchenko V. Mössbauer, Magnetization and X-Ray Diffraction Characterization Methods for Iron Oxide Nanoparticles. *J. Magn. Mater.* **2015**, *380*: 111-116.

[139] Luo P., Bailey E.H., Mooney S.J. Quantification of Changes in Zero Valent Iron Morphology Using X-Ray Computed Tomography. *J. Environ. Sci.* **2013**, *25*: 2344-2351.

[140] Contour J.P., Massies J., Fronius H., Ploog K.J. An XPS Study of the Passivating Oxide Layer Produced on GAA(s)(001) Substrate by Heating in Air Above 200 °C. *Jap. J. Appl. Phys.* **1998**, *27*(2): L167.

[141] Fairley N., Carrick A. The Casa Cookbook – Part 1: Recipes for XPS data Processing. Cheshire: Acolyte Science, **2005**.

[142] Ramos M.A.V., Yan W., Li X-G., Zhang W.X. Simultaneous Oxidation and Reduction of Arsenic by Zero-Valent Iron Nanoparticles: Understanding the Significance of the Core-Shell Structure. *J. Phys. Chem. C* **2009**, *113*(33): 14591-14594.

[143] Joos A., Rümenapp C., Wagner F.E., Gleich B. Characterisation of Iron Oxide Nanoparticles by Mössbauer Spectroscopy at Ambient Temperature. *J. Magn. Mater.* **2016**, *399*: 123-129.

[144] Topical Collection on: *Proc. Int. Conf. on the Applications of the Mössbauer Effect (ICAME 2015)*, Hamburg, Germany, **2015**.

[145] Eljamal R., Eljamal O., Khalil A.M.E., Saha B.B., Matsunaya N. Improvement of the Chemical Synthesis Efficiency of Nanoscale Zero-Valent Iron Particles. *J. Environ. Chem. Eng.* **2018**, *6*(4): 4727-4735.

[146] Carpenter E.E., Calvin S., Stroud R.M., Harris V.G. Passivated Iron as Core-Shell Nanoparticles. *Chem. Mater.* **2003**, *15*: 3245-3246.

[147] Cornell R.M., Schwertmann U. *The Iron Oxides*. 2nd ed., Weinheim: J. Wiley, **2003**.

[148] Chen L., Jin S., Fallgren P.H., Liu F., Colberg P.J.S. Passivation of Zero-Valent Iron and Transport in Porous Media. *Sci. Total Environ.* **2010**, *408*: 2260-2267.

[149] Gatcha-Bandjun N., Noubactep C., Loura B.B. Mitigation of Contamination in Effluents by Metallic Iron: The Role of Iron Corrosion Products. *Environ. Technol. Innov.* **2017**, *8*: 71-83.

[150] Tepong-Tsinde R., Phukan M., Nasi A., Noubactep C., Ruppert R. Validating the Efficiency of the MB Discoloration Method for the Characterization of Fe⁴⁺/H₂O Systems Using Accelerated Corrosion by Chloride Ions. *Chem. Eng. J.* **2015**, *279*: 353-362.

[151] Baker C., Hasanain S.K., Shah S.I. The Magnetic Behaviour of Iron Oxide Passivated Iron. *J. Appl. Phys.* **2004**, *96*(11): 6657-6662.
[154] Fung K.K., Qin B., Zhang X.X. Passivation of α-Fe Nanoparticle by Epitaxial γ-Fe₂O₃ Shell. *Mat. Sci. Eng. A* **2000**, *286*(1): 135-138.

[155] Foltynowicz Z., Bardenshtein B., Sängerlaub S., Antvorskov H., Kozak W. Nanoscale, Zero Valent Iron Particles for Application as Oxygen Scavenger in Food Packaging. *J. Food Pack. Shelf Life* **2017**, *11*: 74-83

[156] Foltynowicz Z. Nanoiron-Based Composite Oxygen Scavengers for Food Packaging. [in:] *Composites Materials for Food Packaging*. Cirillo G., Kozłowski M.A., Spizzirri U.G. Eds., Beverly: John Wiley and Sons, Inc. and Scrivener Publishing LLC, **2018**, 209-234.

[157] Lee H., Yoo H.-Y., Choi J., Nam I.-H., Lee S., Lee S., Kim J.-H., Lee C., Lee J. Oxidizing Capacity of Perioidate Activated with Iron-based Bimetallic Nanoparticles. *Environ. Sci. Technol.* **2014**, *48*(14): 8086-8093.

[158] He F., Zhao D. Preparation and Characterization of a New Class of Starch-stabilized Bimetallic Nanoparticles for Degradation of Chlorinated Hydrocarbons in Water. *Environ. Sci. Technol.* **2005**, *39*: 3314-3320.

[159] Gheju M. Hexavalent Chromium Reduction with Zero-Valent Iron (ZVI) in Aquatic Systems. *Water Air Soil Pollut.* **2011**, *222*(1-4): 103-148.

[160] Jarrett B.R., Frendo M., Vogan J., Louie A.Y. Size Controlled Synthesis of Dextran Sulphate Coated Iron Oxide Nanoparticles for Magneric Resonance Imaging. *Nanotechnology* **2007**, *18*(3): 22-34.

[161] Tiraferri A., Chen K.-L., Sethi R., Elimelech M. Reduced Aggregation and Sedimentation of Zero-Valent Iron Nanoparticles in the Presence of Guar Gum. *J. Colloid Interface Sci.* **2008**, *324*: 71-79.

[162] Tiraferri A., Sethi R. Enhanced Transport of Zerovalent Iron Nanoparticles in Saturated Porous Media by Guar Gum. *J. Nanopart. Res.* **2009**, *11*: 635-645.

[163] Bezbahru A.N., Krajangep S., Chisholm B.J., Khan E., Bermudez J.J. Entrapment of Iron Nanoparticles in Calcium Alginate Beads for Groundwater Remediation Applications. *J. Hazard. Mater.* **2009**, *166*: 1339-1343.

[164] Hojeong K., Hye-Jin H., Jurì J., Seong-Hye K., Ji-Won Y. Degradation of Trichloroethylene (TCE) by Nanoscale Zero-Valent Iron (nZVI) Immobilized in Alginate Bead. *J. Hazard. Mater.* **2010**, *176*: 1038-1043.

[165] Saleh N., Kim H.J., Phenvat T., Matyjaszewski K., Tilton R.D., Lowry G.V. Ionic Strength and Composition Affect the Mobility of Surface-modified Fe⁰ Nanoparticles in Water Saturated Sand Columns. *Environ. Sci. Technol.* **2008**, *42*: 3349-3355.

[166] He F., Zhao D., Liu J., Roberts C.B. Stabilization of Fe/Pd Nanoparticles with Sodium Carboxymethyl Cellulose for Enhanced Transport and Dechlorination of Trichloroethylene in Soil and Groundwater. *Ind. Eng. Chem.* **2007**, *46*: 29-34.

[167] He F., Zhao D., Paul C. Field Assessment of Carboxymethyl Cellulose Stabilized Iron Nanoparticles for *in situ* Destruction of Chlorinated Solvents in Source Zones. *Water Res.* **2010**, *44*: 2360-2370.

[168] Zhou L., Thanh T.L., Gong J., Kim J.H., Kim E.J., Chang Y.S. Carboxymethyl Cellulose Coating Decreases Toxicity and Oxidizing Capacity of Nanoscale Zerovalent Iron. *Chemosphere* **2014**, *104*: 55-61.

[169] He F., Zhao D. Manipulating the Size and Dispersibility of Zerovalent Iron Nanoparticles by Use of Carboxymethyl Cellulose Stabilizers. *Environ. Sci. Technol.* **2007**, *41*(17): 6216-6221.

[170] Zhu B.-W., Lim T.-T., Feng J. Reductive Dechlorination of 1,2,4-Trichlorobenzene with Palladized Nanoscale FeO Particles Supported on Chitosan and Silica. *Chemosphere* **2006**, *65*: 1137-1143.

[171] Geng B., Jin Z., Li T., Qi X. Kinetics of Hexavalent Chromium Removal from Water by Chitosan-FeO Nanoparticles. *Chemosphere* **2009**, *75*: 825-830.

[172] Esfahani A.R., Firouzi A.F., Sayyad G., Kiasat A., Alidokht L., Khataee A.R. Pb(II) Removal from Aqueous Solution by Polyacrylic Acid Stabilized Zero-Valent Iron Nanoparticles: Process Optimization Using Response Surface Methodology. *Res. Chem. Intermed.* **2014**, *40*: 431-445.

[173] Sirk K.M., Saleh N.B., Phenvat T., Kim H.-J., Dufour B., Ok J., Golas P.L., Matyjaszewski K., Lowry G.V., Tilton R.D. Effect of Adsorbed Polyelectrolytes on Nanoscale Zero Valent Iron Particle Attachment
to Soil Surface Models. *Environ. Sci. Technol.* 2009, 43: 3803-3808.

[174] Hydutsky B.W., Mack E.J., Beckerman B.B., Skluzacek J.M., Mallouk T.E. Optimization of Nano- and Microiron Transport through Sand Columns Using Polyelectrolyte Mixtures. *Environ. Sci. Technol.* 2007, 41: 6418-6424.

[175] Laumann S., Micić V., Hofmann T. Mobility Enhancement of Nanoscale Zero-Valent Iron in Carbonate Porous Media through co-Injection of Polyelectrolytes. *Water Res.* 2014, 250: 70-79.

[176] Phenrat T., Saleh N., Sirk K., Kim H.J., Tilton R., Lowry G. Stabilization of Aqueous Nanoscale Zerovalent Iron Dispersions by Anionic Polyelectrolytes: Adsorbed Anionic Polyelectrolyte Layer Properties and Their Effect on Aggregation and Sedimentation. *J. Nanopart. Res.* 2008, 10(5): 795-814.

[177] Kim H.J. Transport, Reactivity and Fate of Polyelectrolyte Modified Zero Valent Iron Nanoparticles Used for Groundwater Remediation in Heterogeneous Porous Media. PhD Thesis, Carnegie Mellon University, Pittsburgh, PA, USA, 2009.

[178] Quinn J., Geiger C., Clausen C., Brooks K., Coon C., O’Hara S., Krug T., Major D., Yoon W.S., Gavaskar A., Holdsworth T. Field Demonstration of DNAPL Dehalogenation Using Emulsified Zero-Valent Iron. *Environ. Sci. Technol.* 2005, 39: 1309-1318.

[179] Zhu B.-W., Lim T.-T., Feng J. Influences of Amphiphiles on Dechlorination of a Trichlorobenzene by Nanoscale Pd/Fe: Adsorption, Reaction Kinetics, and Interfacial Interactions. *Environ. Sci. Technol.* 2008, 42: 4513-4519.

[180] Zhang M., He F., Hao X. Degradation of Soil-sorbed Trichloroethylene by Stabilized Zero Valent Iron Nanoparticles: Effects of Sorption, Surfactants, and Natural Organic Matter. *Water Res.* 2011, 45: 2401-2414.

[181] Wei Y.T., Wu S.C., Yang S.W., Che C.H., Lien H.L., Huang D.H. Biodegradable Surfactant Stabilized Nano-Scale Zero-Valent Iron for in situ Treatment of Vinyl Chloride and 1,2-Dichloroethane. *J. Hazard. Mater.* 2012, 211-212: 373-380.

[182] Chatterjee S., Lim S.-R., Woo S.H. Removal of Reactive Black 5 by Zero-Valent Iron Modified with Various Surfactants. *Chem. Eng. J.* 2010, 160: 27-32.

[183] Krajangpan S., Kalita H., Chisholm B.J., Bezbarua A.N. Iron Nanoparticles Coated with Amphiphilic Polysiloxane Graft Copolymers: Dispersibility and Contaminant Treatability. *Environ. Sci. Technol.* 2012, 46(18): 10130-10136.

[184] Fan G., Cang L., Qin W., Zhou C., Gomes H.I., Zhou D. Surfactants-enhanced Electrokinetic Transport of Xanthan Gum Stabilized Nano Pd/Fe for the Remediation of PCBs Contaminated Soils. *Sep. Purif. Technol.* 2013, 114: 64-72.

[185] Peltier R., Siah W.R., Williams G.V.M., Brimble M.A., Tilley R.D., Wiliams D.E. Novel Phosphour-Peptides as Surface Active Agents in Iron Nanoparticle Synthesis. *Aust. J. Chem.* 2012, 65(6): 680-685.

[186] Xie L., Shang C. Role of Humic Acid and Quinine Model Compounds in Bromated Reduction by Zerovalent Iron. *Environ. Sci. Technol.* 2005, 39(4): 1092-1100.

[187] Dong H., Lo I.M.C. Influence of Humic Acid on the Colloidal Stability of Surface Modified Nano Zero-Valent Iron. *Water Res.* 2013, 47(1): 419-427.

[188] Choi H., Souhail R., Al-Abed Agarwal S., Dionysios D., Dionysiou D.D. Synthesis of Reactive Nano-Fe/ Pd Bimetallic System-Impregnated Activated Carbon for the Simultaneous Adsorption and Dechlorination of PCBs. *Chem. Mater.* 2008, 20(11): 3649-3655.

[189] Baikousi M., Georgiou Y., Daikopoulos C., Bourlinos A.B., Filip J., Zbořil R., Deligiannakis Y., Karakassides M. Synthesis and Characterization of Robust Zero Valent Iron/Mesoporous Carbon Composites and Their Applications in Arsenic Removal. *Carbon* 2015, 93: 636-647.

[190] Zou Y.D., Cao X.H., Luo X.P., Liu Y., Hua R., Liu Y.-H., Zhang Z.-B. Recycle of U(VI) from Aqueous Solution by situ Phosphorylation Mesoporous Carbon. *J. Radioanal. Nucl. Chem.* 2015, 306: 515-525.

[191] Xiao J., Gao B., Yue Q., Sun Y., Kong J., Gao Y., Li Q. Characterization of Nanoscale Zero-Valent Iron
The effective removal of organic and inorganic contaminants using compositions...

[193] Beckingham B., Ghosh U. Field-scale Reduction of PCB Bioavailability with Activated Carbon Smendment to River Sediments. Environ. Sci. Technol. 2011, 45: 10567-10574.

[194] Ren X.M., Li J.X., Tan X.L., Wang X.K. Comparative Study of Graphene Oxide, Activated Carbon and Carbon Nanotubes as Adsorbents for Copper Decontamination. Dalton Trans. 2013, 42: 5266-5274.

[195] Xiao J.N., Gao B.Y., Yue Q.Y., Gao Y., Li Q. Removal of Trihalomethanes from Reclaimed-Water by Original and Modified Nanoscale Zero-Valent Iron: Characterization, Kinetics and Mechanism. Chem. Eng. J. 2015, 262: 1226-1236.

[196] Karabelli D., Unal S., Shahnan T., Eroglu A.E. Preparation and Characterization of Alumina Supported on Granular Activated Carbon and Its Application in Removal of Acrylonitrile from Aqueous Solution. J. Taiwan Inst. Chem. Eng. 2015, 55: 152-158.

[197] Petala E., Dimos K., Douvalis A., Bakas T., Tucek J., Zbořil R., Karakassides M.A. Nanoscale Zero-Valent Iron Supported on Mesoporous Silica: Characterization and Reactivity for Cr(VI) Removal from Aqueous Solution. J. Hazard. Mater. 2013, 261: 295-306.

[198] Zhan J.J., Zheng T., Piringer G., Day C., Mcpherson G.L., Lu Y.F., Papadopoulos K., John V.T. Transport Characteristics of Nanoscale Functional Zerovalent Iron/Silica Composites for in situ Remediation of Trichloroethylene. Environ. Sci. Technol. 2008, 42: 8871-8876.

[199] Li J.S., Li H.J., Zhu Y., Hao Y.X., Sun X.Y., Wang L.J. Dual Roles of Amphiphilic Triblock Copolymer P123 in Synthesis of α-Fe Nanoparticle/Ordered Mesoporous Silica Composites. Appl. Surf. Sci. 2011, 258: 657-661.

[200] Jiang Z., Lv L., Zhang W., Du Q., Pan B., Yang L., Zhang Q. Nitrate Reduction Using Nanosized Zero-Valent Iron Supported by Polystyrene Resins: Role of Surface Functional Groups. Water Res. 2011, 45: 2191-2198.

[201] Shu H.Y., Chang M.C., Chen C.C., Chen P.E. Using Resin Supported Nano Zero-Valent Iron Particles for Decoloration of Acid Blue 113 Azo Dye Solution. J. Hazard. Mater. 2010, 184: 499-505.

[202] Zhao Z., Liu J.-F., Tai C., Zhou Q.F., Hu J.T., Jiang G.B. Rapid Decolorization of Water Soluble Azodyes by Nanosized Zero-Valent Iron Immobilized on the Exchange Resin. Sci. China Series B: Chem. 2008, 51: 186-192.

[203] Xi Y., Megharaj M., Naidu R. Dispersion of Zerovalent Iron Nanoparticles onto Bentonites and Use of These Catalysts for Orange II Decolourisation. Appl. Clay Sci. 2011, 53: 716-722.

[204] Shi L., Lin Y., Zhang X., Chen Z. Synthesis, Characterization and Kinetics of Bentonite Supported nZVI for the Removal of Cr(VI) from Aqueous Solution. Chem. Eng. J. 2011, 171: 612-617.

[205] Zhang Y., Li Y.M., Zheng X.M. Removal of Atrazine by Nanoscale Zero Valent Iron Supported on Organobentonite. Sci. Total Environ. 2011, 409: 625-630.

[206] Li Y.M., Cheng W., Sheng G.D., Li J.F., Dong H.P., Chen Y., Zhu L.Z. Synergetic Effect of a Pillared Bentonite Support on Se(VI) Removal by Nanoscale Zero Valent Iron. Appl. Catal. B 2015, 174-175: 329-335.

[207] Chen Z.X., Jin X.Y., Chen Z., Megharaj M., Naidu R. Removal of Methyl Orange from Aqueous Solution Using Bentonite-supported Nanoscale Zero-Valent Iron. J. Colloid Interface Sci. 2011, 363: 601-607.

[208] Bhowmick S., Chakraborty S., Mondal P., Renterghem W.V., Berghe S.V.D., Ross G.R., Chatterjee D., Iglesias M. Montmorillonite-supported Nanoscale Zero-Valent Iron for Removal of Arsenic from Aqueous Solution. Chem. Eng. J. 2014, 243: 11-23.

[209] Chen C.L., Yang X., Wei J., Tan X.L., Wang X.K. Eu(III) Uptake on Rectorite in the Presence of Humic Acid: A Macroscopic and Spectroscopic Study. J. Colloid Interface Sci. 2013, 393: 249-256.

[210] Yuan N., Zhang G., Guo S., Wan Z. Enhanced Ultrasound Assisted Degradation of Methyl Orange and Metronidazole by Rectorite Supported Nanoscale Zero-Valent Iron. Ultrason. Sonochem. 2016, 228: 62-68.

[211] Üzüm C., Shahwan T., Eroglu A.E., Hallam K.R., Scott T.B., Lieberwirth I. Synthesis and Characterization
of Kaolinite-supported Zero-Valent Iron Nanoparticles and Their Application for the Removal of Aqueous Cu$^{2+}$ and Co$^{2+}$ Ions. *Appl. Clay Sci.* **2009**, *43*: 172-181.

[12] Baltazar S.E., García A., Muñoz-Lira D., Sepúlveda P., Miranda A., Arancibia N.E., Drullinsky D.R. Nanoscale Zero Valent Supported by Zeolite and Montmorillonite: Template Effect of the Removal of Lead Ion from an Aqueous Solution. *J. Hazard. Mater.* **2016**, *301*: 371-380.

[13] Bilardi S., Calabro P.S., Care S., Moraci N., Noubactep C. Improving the Sustainability of Granular Iron/Pumice Systems for Water Treatment. *J. Environ. Manag.* **2013**, *121*: 133-41.

[14] Bilardi S., Calabro P.S., Care S., Moraci N., Noubactep C. Effect of Pumice and Sand on the Sustainability of Granular Iron Beds for the Removal of Cu$^{II}$, Ni$^{II}$, and Zn$^{II}$. *Clean Soil Air Water* **2013**, *41*: 835-843.

[15] Neuwoehner J., Erlenkaemper B., Schofer A., Steinbach K., Hund-Rinke K., Eisentraeger A. Toxicological Characterization of 2,4,6-Trinitrotoluene, Its Transformation Products, and Two Nitramine Explosives. *Environ. Toxicol. Chem.* **2009**, *28*(8): 78-85.

[16] Krol M.M., Oleniuk A.J., Sleep B.E., Bennett P., Xiong Z. A Field Validated Model for *in situ* Transport of Polymer-stabilized n-ZVI and Implications for Subsurface Injection. *Environ. Sci. Technol.* **2013**, *47*(13): 7332-7440.

[17] Krajiangpan S., Jarabek L., Jepperson J., Chisholm B., Bezbarah A. Polymer Modified Iron Nanoparticles for Environmental Remediation. *Polym. Preprints* **2008**, 49: 921-922.

[18] Lachance B., Renoux A.Y., Sarrazin M., Hawari J., Sunahara G.I. Toxicity and Bioaccumulation of Reduced TNT Metabolites in the Earthworm *Eisenia andrei* Exposed to Amended Forest Soil. *Chemosphere* **2004**, *55*(10): 1339-1348.

[19] Cardarelli F. *Materials Handbook: A Concise Desktop Reference.* 2nd ed., New York: Springer, 2008; ISBN 978-1-84628-668-1.

[20] Saleh N., Sirk K., Liu Y., Phenrat T., Dufour B., Matyjaszewski K., Tilton R.D., Lowry G.V. Surface Modifications Enhance Nanoiron Transport and NAPL Targeting in Saturated Porous Media. *Environ. Eng. Sci.* **2007**, *24*: 45-57.

[21] Liu Z., Zhang F., Kent Hoekman S., Liu T., Gai C., Peng N. Homogeneously Dispersed Zerovalent Iron Nanoparticles Supported on Hydrochar-derived Porous Zarbon: Simple, *in situ* Synthesis and Use for Dechlorination of PCBs. *Sustain. Chem. Eng.* **2016**, *2*(6): 3261-3267.

[22] Saleh N., Phenrat T., Sirk K., Dufour B., Ok J., Sarbu T., Matyjaszewski K., Tilton R.D., Lowry G.V. Adsorbed Triblock Copolymers Deliver Reactive Iron Nanoparticles to the Oil/Water Interface. *Nano Lett.* **2005**, *5*(12): 2489-2494.

[23] Chien S., Pieper R., Webster D.C., Singh J. Triblock Copolimers: Synthesis Characterization, and Delivery of a Model Protein. *Inter. J. Pharm.* **2005**, *288*(2): 207-218.

[24] Sun Y.B., Ding C.C., Cheng W.C., Wang X.K. Simultaneous Adsorption and Reduction of U(VI) on Reduced Graphene Oxide-supported Nanoscale Zerovalent Iron. *J. Hazard. Mater.* **2014**, *280*: 399-408.

[25] Sheng G.D., Li Y.M., Yang X., Ren X.M., Yang S.T., Hu J., Wang X.K. Efficient Removal of Arsenate by Versatile Magnetic Graphene Oxide Composites. *RSC Adv.* **2012**, *2*: 12400-12407.

[26] Yang X., Chen C.L., Li J.X., Zhao G.X., Ren X.M., Wang X.K. Graphene Oxide-Iron Oxide and Reduced Graphene Oxide-Iron Oxide Hybrid Materials for the Removal of Organic and Inorganic Pollutants. *RSC Adv.* **2012**, *2*(23): 8821-8826.

[27] Hu J., Yang G.T., Wang X.K. Adsorption of Cu(II) on β-Cyclodextrin Modified Multiwall Carbon Nanotube/Iron Oxides in the Absence/Presence of Fulvic Acid. *J. Chem. Technol. Biotechnol.* **2012**, *87*: 673-681.

[28] Shao D.D., Chen C.L., Wang X.K. Application of Polyaniline and Multiwalled Carbon Nanotube Magnetic Composites for Removal of Pb(II). *Chem. Eng. J.* **2012**, *185-186*: 144-150.

[29] Sheng G.D., Alsaeedi A., Shammakh W., Monaquel S., Sheng J., Wang X.K., Li H., Huang Y.Y. Enhanced Sequestration of Selenite in Water by Nanoscale Zero Valent Iron Immobilization on Carbon Nanotubes by a Combined Batch, XPS and XAFS Investigation. *Carbon* **2016**, *99*: 123-130.

[30] Wen T., Wu X.L., Tan X.L., Wang X.K., Xu A.W. One-pot Synthesis of Water-swellable Mg-Al Layered...
Double Hydroxides and Graphene Oxide Nanocomposites for Efficient Removal of As(V) from Aqueous Solutions. *ACS Appl. Mater. Interfaces* 2013, 5: 3304-3311.

[231] Tan X.L., Fang M., Ren X.M., Mei H.Y., Shao D.D., Wang X.K. Effect of Silicate on the Formation and Stability of Ni-Al LDH at the gamma-Al2O3 Surface. *Environ. Sci. Technol.* 2014, 48: 13138-13145.

[232] Liu M.H., Wang Y.H., Chen L.T., Zhang Y., Lin Z. Mg(OH): Supported Nanoscale Zero Valent Iron Enhancing the Removal of Pb(II) from Aqueous Solution. *ACS Appl. Mater. Interfaces* 2015, 7: 7961-7969.

[233] Zhao Y., Zhao D.L., Chen C.L., Wang X.K. Enhanced Photoreduction and Removal of Cr(VI) on Reduced Graphene Oxide Decorated with TiO2 Nanoparticles. *J. Colloid Interface Sci.* 2013, 405: 211-217.

[234] Kim S.A., Kannan S.K., Lee K.J., Park Y.J., Shea P.J., Lee W.H., Kim H.M., Oh B.T. Removal of Pb(II) from Aqueous Solution by a Zeolite-Nanoscale Zero-Valent Iron Composite. *Chem. Eng. J.* 2013, 217: 54-60.

[235] Cattaneo M.V., Pennington J.C., Brannon J.M., Gunnison D., Harrelson D.W., Zakikhani M. Natural Attenuation of Explosives. [in:] *Remediation of Hazardous Waste Contaminated Soils*. New York: Marcel Dekker, 2000.

[236] Bian S.W., Mudunkotuwa I.A., Rupasinghe T., Grassian V.H. Aggregation and Dissolution of 4 nm ZnO Nanoparticles in Aqueous Environments: Influence of pH, Ionic Strength, Size, and Adsorption of Humic Acid. *Langmuir* 2011, 27: 6059-6068.

[237] Ryu A., Jeong S., Jang A., Choi H. Reduction of Highly Concentrated Nitrate Using Nanoscale Zero-Valent Iron: Effects of Aggregation and Catalyst on Reactivity. *Appl. Catal. B: Environ.* 2011, 105: 128-135.

[238] Shimmin R.G., Schoch A.B., Braun P.V. Polymer Size and Concentration Effects on the Size of Gold Nanoparticles Capped by Polymeric Thiols. *Langmuir* 2004, 20(13): 5613-5620.

[239] Signorini L., Pasquini L., Savini L., Carboni R., Boscherini F., Bonetti E., Giglia A., Pedio M., Mahne N., Nannarone S. Size-dependent Oxidation in Iron/Iron Oxide Core-Shell Nanoparticles. *Phys. Rev. B* 2003, 68: 195423/1-8.

[240] Noubactep C., Care S. Dimensioning Metallic Iron Beds for Efficient Contaminant Removal. *Chem. Eng. J.* 2010, 163: 454-460.

[241] Jandacka P., Alexa P., Pistora J., Li J., Vojtkova H., Hendrych A. Size Distributions of Nanoparticles from Magnetotactic Bacteria as Signatures of Biologically Controlled Mineralization. *Am. Minerol.* 2015, 98: 2105-2114.

[242] Dong J., Zhao Y., Zhao R., Zhou R. Effects of pH and Particle Size on Kinetics of Nitrobenzene Reduction by Zero-Valent Iron. *J. Environ. Sci.* 2010, 22: 1741-1747.

[243] Hofstetter T.B., Hejman C.G., Haderlein S.B., Holliger C., Schwarzenbach R.P. Complete Reduction of TNT and Other (Poly)nitroaromatic Compounds under Iron-Reducing Substance Conditions. *Environ. Sci. Technol.* 1999, 33(9): 1479-1487.

[244] Kadar E., Tarran G.A., Jha A.N., Al-Subiai S.N. Stabilization of Engineered Zero-Valent Nanoiron with Na-Acrylic Copolymer Enhances Spermatoxicity. *Environ. Sci. Technol.* 2011, 45(8): 3245-3251.

[245] Qiu X., Fang Z., Yan X., Cheng W., Lin K. Chemical Stability and Toxicity of Nanoscale Zero-Valent Iron in the Remediation of Chromium Contaminated Watershed. *Chem. Eng. J.* 2013, 220: 61-66.

[246] Yang G.C.C., Tu H., Hung C. Stability of Nanoiron Slurries and Their Transport in the Subsurface. *Environ. Separ. Purif. Technol.* 2007, 58: 166-172.

[247] Wang C.M., Baer D.R., Amonette J.E., Engelhard M.H., Antony J., Qiang Y. Morphology and Electronic Structure of the Oxide Shell on the Surface of Iron Nanoparticles. *J. Am. Chem. Soc.* 2009, 131: 8824-8829.

[248] Ren L., Zhang J., Li Y., Zhang C. Preparation and Evaluation of Cattail Fiber-based Activated Carbon for 2,4-Dichlorophenol and 2,4,6-Trichlorophenol Removal. *Chem. Eng. J.* 2011, 168(2): 553-561.

[249] Cirwertny D.M., Bransford S.J., Roberts A.L. Influence of the Oxidizing Species on the Reactivity of Iron-based Bimetallic Reductants. *Environ. Sci. Technol.* 2007, 41(12): 3734-3740.

[250] Phelan T.Y., Lemke L.D., Bradford S.A., O’Caroll D.M., Abriola L.M. Influence of Textural and Wettability Variations on Predictions of DNAPL Persistence and Plume Development in Saturated Porous
[251] Kocur C.M., O’Caroll D.M., Sleep B.E. Impact on nZVI Mobility in Porous Media. *J. Contam. Hydrol.* 2013, *145*: 17-25.

[252] Gatcha-Bandjun N., Noubactep C., Loura B.B. Mitigation of Contamination in Effluents by Metallic Iron: The Role of Iron Corrosion Products. *Environ. Technol. Innov.* 2017, *8*: 71-83.

[253] Johnson R.L., Johnson G.O., Nurmi J.T., Tratnyek P.G. Natural Organic Matter Enhanced Mobility of Nano Zerovalent Iron. *Environ. Sci. Technol.* 2009, *43*: 5455-5460.

[254] Noubactep C., Licha T., Scott T.B., Fall M., Sauter M. Exploring the Influence of Operational Parameters on the Reactivity of Elemental Iron Materials. *J. Hazard. Mater.* 2009, *172*: 943-951.

[255] Kubaniova D., Cesnek M., Milkovic O., Kohout J., Miglierini M. Composition of α-Fe Nanoparticles Precipitated from CuFe Alloy Studied by Hyperfine Interactions. *Proc. Int. Conf. on Hyperfine Interaction and their Application (HYPERFINE 2016)*, Lueven, Belgium, 2016.

[256] Huang Y.Y., Liu F., Li H.D. Degradation of Tetrachloromethane and Tetrachloroethene by Ni/Fe Bimetallic Particles. *J. Phys. Conf. Ser.* 2009, *188*(1): 42-49.

[257] Kuang Y., Zhou Y., Chen Z., Megharaj M., Naidu R. Impact of Fe and Ni/Fe Nanoparticles on Biodegradation of Phenol by the Strain *Bacillus fusiformis* (BFN) at Various pH Values. *Bioresour. Technol.* 2013, *136*: 588-594.

[258] Laumann S., Micić V., Hofmann T. Mobility Enhancement of Nanoscale Zero-Valent Iron in Carbonate Porous Media through co-Injection of Polyelectrolytes. *Water Res.* 2014, *250*: 70-79.

[259] Noubactep C. On the Operating Mode of Bimetallic Systems for Environmental Remediation. *J. Hazard. Mater.* 2009, *164*: 394-395.

[260] Alymov M.I., Rubstov N.M., Seplyarski B.S., Zelenski V.A., Ankundinov A.B. Preparation and Characterization of Iron Nanoparticles Protected by an Oxide Film. *Inorg. Mat.* 2017, *53*(9): 911-915.

[261] Lasek J.A. Investigations of the Reduction of NO to N$_2$ by Reaction with Fe under Fuel-rich and Oxidative Atmosphere. *Heat Mass Transf.* 2014, *50*: 933-943.

[262] Balko B.A., Tratnyek P.G. Photoeffects on the Reduction of Carbon Tetrachloride by Zero-Valent Iron. *J. Phys. Chem. B* 1998, *102*: 2936-2945.

[263] Matheson L.J., Tratnyek P.G. Reductive Dehalogenation of Chlorinated Methanes by Iron Metal. *Environ. Sci. Technol.* 1995, *29*: 2936-2945.

[264] Kolditz L. *Inorganic Chemistry.* (in Polish) Warsaw: PWN, 1994; ISBN 83-01-10072-9.

[265] O’Hannesin S.F., Gillham R.W. Long-term Performance of an *in situ* ’Ironwall’ for Remediation of VOCs. *Groundwater* 1998, *36*: 164-170.

[266] Reardon J.E. Anaerobic Corrosion of Granular Iron: Measurement and Interpretation of Hydrogen Rates. *Environ. Sci. Technol.* 1995, *29*: 2936-2945.

[267] Shih Y.H., Hsu C.Y., Su Y.F. Reduction of Hexachlorobenzene by Nanoscale Zerovalent Iron: Kinetics, pH Effect, and Degradation Mechanism. *Separ. Purif. Technol.* 2011, *76*: 268-274.

[268] Shen J.M., Chen Z.L., Xu Z.Z., Li X.Y., Xu B.B., Qi F. Kinetics and Mechanism of Degradation of p-Chloronitrobenzene in Water by Ozonation. *J. Hazard. Mater.* 2008, *152*: 1325-1331.

[269] Sinha A., Bose P. Dehalogenation of 2-Chloronaphthalene by Cast Iron. *Water Air Soil Poll.* 2006, *172*: 375-390.

[270] Tratnyek P.G., Salter A.J. Response to Comment on Degradation of 1,2,3-Trichloropropane (TCP): Hydrolysis, Elimination, and Reduction by Iron and Zinc. *Environ. Sci. Technol.* 2010, *44*: 3198-3199.

[271] Balko B.A., Tratnyek P.G. Photoeffects on the Reduction of Carbon Tetrachloride by Zero-Valent Iron. *J. Phys. Chem. B* 1998, *102*: 1459-1465.

[272] Matheson L.J., Tratnyek P.G. Reductive Dehalogenation of Chlorinated Methanes by Iron Metal. *Environ. Sci. Technol.* 28: 2045-2053.
The effective removal of organic and inorganic contaminants using compositions...

[274] Deng B., Hu S. Reductive Dechlorination of Chlorinated Solvents on Zerovalent Iron Surfaces. [in:] Physicochemical Groundwater Remediation. Smith J.A., Burns S.E. Eds., New York: Kluwer Academic, 2001, pp. 139-159; ISBN 978-0-306-46928-2.

[275] Gillham R.W., O’Hannesin S.F. Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron in Ground Water. Groundwater 1994, 32: 958-967.

[276] Orth W.S., Gillham R.W. Dechlorination of Trichloroethene in Aqueous Solution Using Fe\(^0\). Environ. Sci. Technol. 1996, 30: 66-71.

[277] Liang L., Gu B., Yin X. Removal of Technetium-99 from Contaminated Groundwater with Sorbents and Reductive Materials. Sep. Technol. 1996, 6: 111-122.

[278] Puls R.W., Paul C.J., Powell R.M. The Application of in situ Permeable Reactive (Zero-Valent Iron) Barrier Technology for the Remediation of Chromate-contaminated Groundwater: A Feld Test. Appl. Geochem. 1999, 14: 989-1000.

[279] Bojic A., Bojic D., Andjelkovic T. Removal of Cu\(^{2+}\) and Zn\(^{2+}\) from Model Wastewaters by Spontaneous, Reduction-Coagulation Process in Flow Conditions. J. Hazard. Mater. 2009, 168: 813-819.

[280] Noubactep C. A Critical Review on the Mechanism of Contaminant Removal in Fe\(^0\)-H\(_2\)O Systems. Environ. Technol. 2008, 29: 909-920.

[281] Noubactep C. Investigating the Processes of Contaminant Removal in Fe\(^0\)/H\(_2\)O Systems. Korean J. Chem. Eng. 2012, 29: 1050-1056.

[282] Ramos M.A.V., Yan W., Li X.-Q., Koel B.E., Zhang W.-X. Simultaneous Oxidation and Reduction of Arsenic by Zero-Valent Iron Nanoparticles: Understanding the Significance of the Core-Shell Structure. J. Phys. Chem.C 113(33): 14591-14594.

[283] Ludwig R.D., Su C., Lee T.R., Wilkin R.T., Acree S.D., Ross R.R., Keeley A. In situ Chemical Reduction of Cr(VI) in Groundwater Using a Combination of Ferrous Sulfate and Sodium Dithionite: A Feld Investigation. Environ. Sci. Technol. 2007, 41: 5299-5305.

[284] Bojic A., Purenovic M., Bojic D. Removal of Chromium(VI) from Water by Micro-Alloyed Aluminium Based Composite in Flow Conditions. Water SA 2004, 30: 353-359.

[285] Ding C.C., Cheng W.C., Sun B., Wang X.K. Effects of Bacillus subtilis on the Reduction of U(VI) by Nano-Fe(0). Geochim. Cosmochim. Acta 2015, 165: 86-107.

[286] Sun Y.B., Ding C.C., Cheng W.C., Wang X.K. Simultaneous Adsorption and Reduction of U(VI) on Reduced Graphene Oxide-supported Nanosacle Zerovalent Iron. J. Hazard. Mater. 2014, 280: 399-408.

[287] Isac L., Arnáiz C. Biomass Characterization and Biological Activity Tests in Wastewater Treatment. (in Spanish) Afinidad. 2005, 62(517): 197-210.

[288] Fajardo C., Saccà M.L., Martinez-Gomariz M., Costa G., Nande M., Martin M. Transcriptional and Proteomic Stress Responses of a Soil Bacterium Bacillus cereus to Nanosized Zero-Valent Iron (nZVI) Particles. Chemosphere 2013, 93(6): 1077-1083.

[289] Fajardo C., Ortiz L.T., Rodriguez-Membibre M.L., Nande M., Lobo M.C., Martin M. Assessing the Impact of Zero-Valent Iron (ZVI) Nanotechnology on Soil Microbial Structure and Functionality: A Molecular Approach. Chemosphere 2012, 86(8): 802-808.

[290] Bruton T.A., Halden R.U., Rolf U. Effect of Nanoscale Zero-Valent Iron Treatment on Biological Reductive Dechlorination, A Review of Current Understanding and Research Needs. Crit. Rev. Environ. Sci. Technol. 2014, 45(11): 1148-1175.

[291] Chen K.F., Yeh T.Y., Kao C.M., Sung W.P., Lin C.C. Application of Nanoscale Zero-Valent Iron (nZVI) to Enhance Microbial Reductive Dechlorination of TCE: A Feasibility Study. Curr. Nanosci. 2012, 8(1): 55-59.

[292] Huang L., Shi Y., Wang N., Dong Y. Anaerobic/Aerobic Conditions and Biostimulation for Enhanced Chlorophenols Degradation in Biocathode Microbial Fuel Cells. Biodegradation 2014, 25: 615-632.
Environ. Sci. Technol. 2010, 44: 3474-3480.

[294] Shin K., Cha D.K. Microbial Reduction of Nitrate in the Presence of Nanoscale Zero-Valent Iron. Chemosphere 2008, 72: 257-262.

[295] Liu Y., Li S., Chen Z., Megharaj M., Naidu R. Influence of Zero-Valent Iron Nanoparticles on Nitrate Removal by Paracoccus sp. Chemosphere 2014, 108: 426-432.

[296] Doutsova K.M., Pennington J.C., Hayes C., Simunek J., Willisford C.W. Dissolution and Transport of 2,4-DNT and 2,6-DNT from M1 Propellant in Soil. Chemosphere 2009, 77(4): 597-603.

[297] Göttinger A.M., McMartin D.W., Wild D.J., Moldovan B. Integration of Zero Valent Iron Sand Beds into Biological Treatment Systems for Uranium Removal from Drinking Water Wells in Rural Canada. Can. J. Civ. Eng. 2013, 40: 945-950.

[298] Jagadevan S., Jayamurthy M., Dobson P., Thompson I.P. A Novel Hybrid Nano Zerovalent Iron Initiated Oxidation-Biological Degradation Approach for Remediation of Recalcitrant Waste Metalworking Fluids. Water Res. 2012, 46(7): 2395-2404.

[299] Pokhrel D., Viraraghavan T. Biological Filtration for Removal of Arsenic from Drinking Water. J. Environ. Manag. 2009, 90: 1956-1961.

[300] Camargo P.H.C., Satyanarayana K.G., Wypych F. Nanocomposites: Synthesis, Structure, Propertiers and New Application Opportunities. Mater. Res. 2009, 12(1): 1-39.

[301] Beristain-Montiel L., Gómez J., Monroy O., Cuervo-López F.M., Ramírez-Vives F. Biodegradation of 2-Chlorophenol (2CP) in an Anaerobic Sequencing Batch Reactor (ASBR). Environ. Sci. Technol. 2012, 46(10): 1721-1728.

[302] You Y., Han J., Chiu P.C., Jin Y. Removal and Inactivation of Waterborne Viruses Using Zero Valent Iron. Environ. Sci. Technol. 2005, 39: 9263-9269.

[303] Li Z., Greden K., Alvarez P.J.J., Gregory K.B., Lowry G.V. Adsorbed Polymer and NOM Limits Adhesion and Toxicity of Nano Scale Zerovalent Iron to Escherichia coli. coli. Environ. Sci. Technol. 2010, 44: 3462-3467.

[304] Kim J.V., Park J.K., Lee C., Nelson K.L., Yoon J. Inactivation of Escherichia coli by Nanoparticulate Zero-Valent Iron an Ferrousian. Appl. Environ. Microbiol. 2010, 76: 7668-7662.

[305] Lee C., Kim J.Y., Lee W.I., Nelson K.L., Yoon J., Sedlak D.L. Bactericidal Effect of Zerovalent Iron Nanoparticles on Escherichia coli. Environ. Sci. Technol. 2008, 42: 4927-4933.

[306] Lovley D.R., Stoltz J.F., Nord Jr. G.L., Phillips E.J.P. Anaerobic Production of Magnetite by Dissimilatory Iron-reducing Microorganism. Nature 1987, 330(6145): 252-254.

[307] Liu J., Vipulandan C., Cooper T.T., Vipulandan G. Effect of Nanoparticles on Biosurfactant Production. J. Nanoparticles Res. 2013, 1: 4927-4933.

[308] Craig H.D., Sisk W.E., Nelson M.D., Dana W.H. Bioremediation of Explosives-contaminated Soils: A Status Review. Manhattan (KS): Great Plains and Rocky Mountain Hazardous Substance Research Center, Kansas State University, 1995, 164.

[309] Nejidat A., Kafka L., Tekoaeh Y., Ronen Z. Effect of Organic and Inorganic Nitrogenous Compounds on RDX Degradation and Cytochrome P-400 Expression in Rhodococcus strain YH1. Biodegradation 2008, 19(8): 13-320.

[310] Bojic A., Purenovic M., Bojic D., Andjelkovic T. Dehalogenation of Trihalomethanes by a Micro-Alloyed Aluminium Composite under Flow Conditions. Water SA 2007, 33(2): 297-304.

[311] Babuponnusami A., Muthukumar K. Removal of Phenol by Heterogenous Photo Electro Fenton-like Process Using Nano-Zero Valent Iron. Separ. Purif. Technol. 2012, 98: 130-135.

[312] Birke V., Schuett C., Burmeier H., Friedrich H.-J. Impact of Trace Elements and Impurities in Technical Zero-Valent Iron Brands on Reductive Dechlorination of Chlorinated Ethenes in Groundwater. [in:] Permeable Reactive Barrier, Sustainable Groundwater Remediation. Naidu R., Birke V. Eds., Boca Raton/London/New York: CRC Press, 2014, pp. 87-98; ISBN-13 978-4822-2447-4.

[313] Lien H.L., Zhang W.X. Nanoscale Iron Particles for Complete Reduction of Chlorinated Ethenes. Colloids Surf. A: Physicochem. Eng. Aspects 2001, 191: 97-105.
[314] Liu Y.Q., Majetich S.A., Tilton R.D., Sholl D.S., Lowry G.V. TCE Dechlorination Rates, Pathways, and Efficiency of Nanoscale Iron Particles with Different Properties. *Environ. Sci. Technol.* **2005**, *39*: 1338-1345.

[315] Liu Y., Phenrat T., Lowry G.V. Effect of TCE Concentration and Dissolved Groundwater Solute on nZVI-promoted TCE Dechlorination and H₂ Evolution. *Environ. Sci. Technol.* **2007**, *41*: 7881-7887.

[316] Liu Y., Shen J.M., Chen Z.L., Liu Y. Degradation of p-Chloronitrobenzene in Drinking Water by Manganese Silicate Catalyzed Ozonation. *Desalination* **2011**, *279*: 219-224.

[317] Shu H.Y., Chang M.C., Chen C.C., Chen P.E. Using Resin Supported Nano Zero-Valent Iron Particles for Decoloration of Acid Blue 113 Azo Dye Solution. *J. Hazard. Mater.* **2010**, *184*: 499-505.

[318] Shu H.Y., Chang M.C., Yu H.H., Chen W.H. Reduction of an Azo Dye Acid Black 24 Solution Using Synthesized Nanoscale Zero-valent Iron Particles. *J. Colloid Interface Sci.* **2007**, *314*: 89-97.

[319] Poursaberi T., Konoz E., Sarrafi A.H.M., Hassanisadi M., Hajifathli F. Application of Nanoscale Zero-Valent Iron in the Remediation of DDT from Contaminated Water. *Chem. Sci. Trans.* **2012**, *1*: 658-668.

[320] El-Temsah Y.S., Joner E.J. Effects of Nano-Sized Zero-Valent Iron (nZVI) on DDT Degradation in Soil and Its Toxicity to Collembola and Ostracods. *Chemosphere* **2013**, *92*(1): 131-137.

[321] Wang L., Yang J., Li Y.M., Lv J., Zou J. Removal of Chlorpheniramine in a Nanoscale Zero-Valent Iron Induced Heterogeneous Fenton System: Influencing Factor Sand Degradation Intermediates. *Chem. Eng. J.* **2016**, *284*: 1058-1067.

[322] Fang Z.Q., Chen J.H., Qiu X.H., Qiu X.Q., Cheng W., Zhu L.C. Effective Removal of Antibiotic Metronidazole from Water by Nanoscale Zero-Valent Iron Particles. *Desalination* **2011**, *268*: 60-67.

[323] Fang Z., Qiu X., Chen J., Qiu X. Degradation of Metronidazole by Nanoscale Zero-Valent Metal Prepared from Steel Pickling Waste Liquor. *Appl. Catal. B: Environ.* **2010**, *100*(1-2): 221-228.

[324] Chen J.H., Qiu X.Q., Fang, Z.Q., Yang M., Pokeung T., Gu F.L., Cheng W., Lan B.Y. Removal Mechanism of Antibiotic Metronidazole from Aquatic Solutions by Using Nanoscale Zero-Valent Iron Particles. *Chem. Eng. J.* **2012**, *181-182*: 113-119.

[325] Chen H., Luo H.J., Lan Y.C., Dong T.T., Hu B.J., Wang Y.P. Removal of Tetracycline from Aqueous Solutions Using Polyvinylpyrrolidone (PVP-K30) Modified Nanoscale Zero-Valent Iron. *J. Hazard. Mater.* **2011**, *192*: 44-53.

[326] Babuponnusami A., Muthukumar K. Removal of Phenol by Heterogenous Photo Electro Fenton-like Process Using Nano-Zero-Va lent Iron. *Separ. Purif. Technol.* **2012**, *98*: 130-135.

[327] Iurascu B., Siminiceanu J., Vione D., Vicente M.A., Gil A. Phenol Degradation in Water through a Heterogeneous Photo-Fenton Process Catalysed by Fe-treated Laponite. *Water Res.* **2009**, *43*(5): 1313-1322.

[328] Liao C.J., Chung T.L., Chen W., Kuo S.L. Treatment of Pentachlorophenol-contaminated Soil Using Nano-scale Zero-Valent Iron with Hydrogen Peroxide. *J. Mol. Catal. A: Chem.* **2007**, *265*: 189-194.

[329] Calderon B., Aracil I., Fullana A. Deodorization of a Gas Stream Containing Dimethyl Disulfide with Zero-Valent Iron Nanoparticles. *Chem. Eng. J.* **2012**, *183*: 325-331.

[330] Hu J., Lo I.M.C., Chen G. Removal of Cr(VI) by Magnetite Nanoparticle. *Water Sci. Technol.* **2004**, *50*(12): 139-146.

[331] Lv X., Xu J., Jiang G., Tang J., Cut X. Highly Active Nanoscale Zero-Valent Iron (nZVI)-Fe₃O₄ Nanocomposites for the Removal of Chromium(VI) from Aqueous Solutions. *J. Colloid Interface Sci.* **2012**, *369*(1): 460-469.

[332] Bose P., Glaze W.H., Maddox D.S. Degradation of RDX by Various Advanced Oxidation Processes: II. Organic by-Products. *Water Res.* **1998**, 32(4): 1005-1018.

[333] Ponder S.M., Darab J.G., Mallouk T.E. Remediation of Cr(VI) and Pb(II) Aqueous Solutions Using Supported, Nano-Scale Zero-Valent Iron. *Water Sci. Technol.* **2000**, *34*: 2564-2569.

[334] Selvaran M., Prema P. Removal of Toxic Metal Hexavalent Chromium[Cr(VI)] from Aqueous Solution Using Starch Stabilized Nanoscale Zerovalent Iron as Adsorbent: Equilibrium and Kinetics. *Int. J. Environ. Sci.* **2012**, *2*: 1962-975.
[335] Zou Y., Wang X., Khan A., Wang P., Liu Y., Ahmed A., Hayat T., Wang X. Environmental Remediation and Application of Nanoscale Zerovalent Iron and its Composites for the Removal of Heavy Metal Ions: A Review. Environ. Sci. Technol. Crit. Rev. 2016, 50: 7290-7304.

[336] Zhang S.W., Li J. X., Wen T., Xu J.Z., Wang X.K. Magnetic Fe₃O₄@NiO Hierarchical Structures: Preparation and Their Excellent As(V) and Cr(VI) Removal Capabilities. RSC Adv. 2014, 3: 2754-2764.

[337] Esfahani A.R., Firouzi A.F., Sayyad G., Kiasat A., Alidokht L., Khatae A.R. Pb(II) Removal from Aqueous Solution by Polycrylic Acid Stabilized Zero-Valent Iron Nanoparticles: Process Optimization Using Response Surface Methodology. Res. Chem. Intermed. 2014, 40: 431-445.

[338] Boparai H.K., Joseph M., O’Carroll D.M. Cadmium (Cd²⁺) Removal by Nano Zero-Valent Iron: Effects of Solution Chemistry and Surface Complexation Modelling. Environ. Sci. Pollution Res. 2013, 20(9): 6210-6221.

[339] Boparai H.K., Joseph M., O’Carroll D.M. Kinetics and Thermodynamics of Cadmium Ion Removal by Adsorption on Nano Zero-Valent Iron Particles. J. Hazard. Mater. 2011, 186(1): 458-465.

[340] Nazli E. Characterization of the Adsorption Behavior of Aqueous Cd(II) and Ni(II) Ions on Nanoparticles of Zero-Valent Iron. Master’s Thesis, School of Engineering and Science of Izmir Institute of Technology, Turkey, 2008.

[341] Morgada M.E., Levy I.K., Salomone V., Farias S.S., Lopez G., Litter I.M. Arsenic(V) Removal with Nanoparticulate Zerovalent Iron: Effect of UV Light and Humic Acids. Catal. Today 2009, 143(3-4): 261-268.

[342] Kanel S.R., Nepal D., Manning B., Choi H. Transport of Surface-modified Iron Nanoparticle in Porous Media and Application to Arsenic(III) Remediation. J. Nanopart. Res. 2007, 9: 725-735.

[343] Bang S., Johnson M.D., Korfiatis G.P., Meng X. Chemical Reaction Between Arsenic and Zero-Valent Iron. Water Res. J. 2005, 39(5): 763-770.

[344] Giasuddin A.B., Kanel S.R., Choi H. Adsorption of Humic Acid onto Nanoscale Zerovalent Iron and Its Effect on Arsenic Removal. Environ. Sci. Technol. 2007, 41: 2022-2027.

[345] Kanel S.R., Grenache J.-M., Choi H. Arsenic(V) Removal from Groundwater Using Nano Scale Zero-Valent Iron as a Colloidal Reactive Barrier Material. Environ. Sci. Technol. 2006, 40(6): 2045-2050.

[346] Kanel S.R., Manning B., Charlet L., Choi H. Removal of Arsenic(III) from Groundwater by Nanoscale Zero-Valent Iron. Environ. Sci. Technol. 2005, 39: 1291-1298.

[347] Tyrovola K., Peroulaki E., Nikolaidis N.P. Modeling of Arsenic Immobilization by Zero Valent Iron. Eur. J. Soil Biol. 2007, 43(5-6): 356-367.

[348] Ramos M.A V., Yan W., Li X.-G., Koel B.E., Zhang W.X. Simultaneous Oxidation and Reduction of Arsenic by Zero-Valent Iron Nanoparticles: Understanding the Significance of the Core-Shell Structure. J. Phys. Chem. C 2009, 113(33): 14591-14594.

[349] Ling L., Zhang W.-x. Sequestration of Arsenate in Zero-Valent Iron Nanoparticles: Visualisation of Intraparticle Reactions at Angstrom Resolutions. Environ. Sci. Technol. Lett. 2014, 1(7): 305-309.

[350] Olegario J.T., Yee N., Miller M., Szczepaniak J., Manning B. Reduction of Se(VI) to Se(–II) by Zerovalent Iron Nanoparticle Suspensions. J. Nanopart. Res. 2010, 12: 2057-2068.

[351] Cao J., Elliott D., Zhang W.-X. Perchlorate Reduction by Nanoscale Iron Particles. J. Nanoparticle Res. 2005, 7(4-5): 499-506.

[352] Hsu J., Liao C., Lin C., Weng S.C. Effect of Precursor Concentration on the Characteristics of Nanoscale Zerovalent Iron and Its Reactivity of Nitrate. Water Res. 2006, 40: 2485-2492.
[356] Martel R., Robertson T.J., Quan D.M. 2,4,6-Trinitrotoluene in Soil and Ground Water under a Waste Lagoon at the Former Explosives Factory Maribyrnong (EFM), Victoria, Australia. Environ. Geology 2008, 53(6): 1249-1259.

[357] Choe S., Chang Y.Y., Hwang K.Y., Khim J. Kinetics of Reductive Denitrification by Nanoscale Zero-Valent Iron. Chemosphere 2000, 41: 1307-1311.

[358] Almeelbi T., Bezbarah A. Aqueous Phosphate Removal Using Nanoscale Zero-Valent Iron. J. Nanopart. Res. 2012, 14: 3-14.

[359] Alfred B.J., Racharaks R. Laboratory Comparison of Four Iron-based Filter Materials for Drainage Water Phosphate Treatment. Water Environ. Res. 2014, 86: 852-862.

[360] Albright R.D. Death of the Chesapeake: A History of the Military’s Role in Polluting the Bay. Scrivener Publishing, J. Willey, 2012; ISBN 978-1-118-68627-0.

[361] Phillips C.T., Checkai R.T., Wentsel R.S. Toxicity of Selected Munitions and Munition Contaminated Soil on the Earthworm (Eisenia foetida). U.S. Army Chemical and Biological Defence Agency, Report ERDEC-TR-037, Edgeworth Research Development and Engineering Center, Aberdeen Proving Ground, MD, 1993.

[362] ATSDR. Toxicological Profile for 2,4,6-Trinitrotoluene. Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA, 1995.

[363] Xue S.K., Iskandar I.K., Selim H.M. Adsorptiondesorption of 2,4,6-Trinitrotoluene and Hexahydro-1,3,5-trinitro-1,3,5-triazine in Soils. Soil Sci. 1995, 160(5): 317-327.

[364] Butler E.C., Hayes K.F. Effects of Solution Composition and pH on the Reductive Dechlorination of Hexachloroethane by Iron Sulfide. Environ. Sci. Technol. 1998, 32: 1276-1284.

[365] Zoch K.D., Stennstrom M.K. Fenton Oxidation of Heksahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and Octahydro-1,3,5-tetranitro-tetrazocine (HMX). Water Res. 2002, 36: 1331-1341.

[366] Brannon M., Myers T.E. Review of Fate and Transport Processes of Explosives. U.S. Army Corps of Engineers, Technical Report IRRP-97-2, US, 1997.

[367] ATSDR. To SDR. Toxicological Profile for HMX. Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA, 1997.

[368] Harley S.D., Fellows R.J., Campbell J.A., Cataldo D.A. Determination of the Explosive 2,4,6-Trinitrophenylmethylnitrate and Transformation Products in Soil. J. Chromatography 1991, 605: 227-240.

[369] Coleman N.V., Spain J.C., Duxbury T. Evidence that RDX Biodegradation by Rhadococcus DN 22, is Plasmid Borne and Involves a Cytochrome P-450. J. Appl. Microbiol. 2002, 98: 463-472.

[370] Bandstra J.Z., Miehr R., Johnson R.L., Tratnyek P.G. Reduction of 2,4,6-Trinitrotoluene by Iron Metal Kinetic Controls on Product Distributions in Batch Experiments. Environ. Sci. Technol. 2005, 39(1): 230-238.

[371] Carr R.C., Nipper M. Development of Marine Sediment Toxicity Data for Ordnance Compounds and Toxicity Identification Evaluation Studies at Select Naval Facilities. Naval Facilities Engin. Comm., Report CR 01-002-ENV, US, 2000.

[372] Kim J.S., Shea P.J., Yang J.E., Kim J.E. Halide Salts Accelerate Degradation of High Explosives by Zero-Valent Iron. Environ. Pollut. 2007, 147: 634-641.

[373] MacDonald J.A., Small M.J., Morgan M.G. Quantifying the Risks of Unexploded Ordnance at Closed Military Bases. Environ. Sci. Technol. 2009, 43(2): 259-265.

[374] Douglas T.A., Walsh M.E., McGrath C.J., Weiss C.A., Jaramillo A.M., Trainor T.P. Desorption of Nitramine and Nitroaromatic Explosive Residues from Soils Detonated under Controlled Conditions. Environ. Toxicol. Chem. 2010, 30(2): 345-353.

[375] Kalderis D., Juchasz A.L., Boopathy R., Comfort S. Soils Contained with Explosives: Environmental Fate and Evaluation on State of the Art Remediation in Processes. IUPAC Technical Report 83(7), 2001.

[376] McDowall L. Degradation of Toxic Chemicals by Zero-Valent Metal Nanoparticles – A Literature Review. Australian Government Department of Defense, DSTO, 2005.
[377] Islam M.N., Shin M.S., Jo Y.-T., Park H.-J. TNT and RDX Degradation and Extraction from Contaminated Soil Using Subcritical Water. *Chemosphere* 2015, 119: 1448-1152.

[378] Saad R., Thiboutot S., Ampleman G., Dashan W., Hawari J. Degradation of Trinitroglycerin (TNG) Using Zero-Valent Iron Nanoparticles/Nanosilica SBA-15 Composite (ZVINs/SBA-15). *Chemosphere* 2010, 81: 853-858.

[379] Hundal L.S., Singh J., Bier E.L., Shea P.J., Compart S.D., Powers W.L. Removal TNT and RDX from Water and Soil Using Iron Metal. *Environ. Pollut.* 1997, 97(1-2): 55-64.

[380] Glover D.J., Hoffsommer J.C. *Photolysis of RDX: Identification and Reaction Products.* Naval Surface Weapons Center, Technical Report NSWCTR-79-349, Silver Spring, MD, 1979.

[381] Lavine B.K., Auslander G., Ritter J. *Polarographic Studies of Zero Valent Iron as a Reductant for Remediation of Nitroaromatics in the Environment.* *Microchem. J.* 2001, 70: 69-83.

[382] Ryon M.G. *Water Quality Criteria for 2,4,6-Trinitrotoluene (TNT).* Oak Ridge National Laboratory, AD ORNL 6304, 1987.

[383] ATSDR. *Toxicological Profile for 2,4,6-Trinitrotoluene.* Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA, 1995.

[384] Simin M., Chechai R.T., Kolakowski J.E., Kuperman R.G., Phillips C.T., Kurnas C.W. Ecological Soil Screening Levels for Plants Exposed to TNT: Supporting Range Sustainability for Training and Testing. *Proc. 25th Army Science Conf. Transformational Army Science and Technology: Charting the Future of S&T for the Soldier*, Orlando, Florida, 2006.

[385] Douglas T.A., Walsh M.E., McGrath C.J., Weiss C.A. Investigating the Fate of Nitroaromatic (TNT) and Nitramine (RDX and HMX) Explosives in Fractured and Pristine Soils. *J. Environ. Quality* 2009, 38(6): 2285-2294.

[386] Zhang M., Liu G.-h., Song K., Wang Z., Zhao Q., Li Z., Ye Z. Biological Treatment of 2,4,6-Trinitrotoluene (TNT) Red Water by Immobilized Anaerobic-Aerobic Microbial Filters. *Chem. Eng. J.* 2015, 259: 876-884.

[387] Ullah H., Shah A.A., Hasan F., Hameed A. Biodegradation of Trinitrotoluene by Immobilized *Bacillus Sp. Yre1*. *Pak. J. Bot.* 2010, 42(5): 3357-3367.

[388] Uchimiya M. Reductive Transformation of 2,4-Dinitrotoluene: Roles of Iron and Natural Organic Matter. *Aquat. Geochem.* 2010, 16: 547-562.

[389] Pichtel J. Distribution and Fate of Military Explosives and Propellants on Soil: A Review. *Appl. Environ. Soil Sci.* 2012, 2012: ID 617236/1-33.

[390] Islam M.N., Shin M.S., Jo Y.-T., Park H.-J. TNT and RDX Degradation and Extraction from Contaminated Soil Using Subcritical Water. *Chemosphere* 2015, 119: 1448-1152.

[391] Walsh M.R., Walsh M.E., Hewitt A.D., Collins C.M. Field-expedient Disposal of Excess Artillery Propellants. *Proc. SERDP&ESTCP’s Partners in Environ. Technol. Tech. Symp. and Workshop*, Washington (D.C.), USA, 2008.

[392] Kim J.B., Cha D.K., Chiu P.C., Oh S.-Y. *Degradation of Energetic Compounds Using Zerovalent Iron (ZVI).* Department of Civil and Environmental Engineering, Final Report ESTCP Project WP-200524, University of Delaware, 2012.

[393] Urbansky E.T. Perchlorate Chemistry: Implications for Analysis and Remediation. *Bioremediation* 1998, 2: 81-95.

[394] Gullick R.Q., Lechvallier M.W., Barhorst T.A.S. Occurrence of Perchlorate in Drinking Water Sources. *J. Amer. Water Works Assoc.* 2001, 93(1): 66-77.

[395] Logan B.E. Assessing the Outlook for Perchlorate Remediation. *Environ. Sci. Technol.* 2001, 35: 482A-487A.

[396] Motzer W.E. Perchlorate: Problems, Detection, and Solutions. *Environ. Forensics* 2001, 2: 301-311.

[397] Trumpolt C.W., Crain M., Cullison C.D., Flanagan S.J., Siegel P.L., Lathrop S. Perchlorate: Sources, Uses, and Occurrences in the Environment. *Remediation* 2005, 16(1): 65-89.

[398] Gębka K., Beldowski J., Beldowska M. The Impact of Military Activities on the Concentration of Mercury
in Soils of Sitting Training Grounds and Marine Sediments. *Environ. Sci. Pollut. Res.* **2016**, *23*(22): 23103-23111.

[399] Xu J., Song Y., Min B., Steinberg L., Logan B.E. Microbial Degradation of Perchlorate: Principles and Applications. *Environ. Eng. Sci.* **2003**, *20*(5): 405-422.

[400] Bordeleau G., Martel R., Ampleman G., Thiboutot S. Environmental Impacts of Training Activities at an Air Weapons Range. *J. Environ. Quality* **2008**, *37*(2): 308-317.

[401] Naftz D.L., Morrison S.J., Davis J.A., Fuller C.C. Introduction to Groundwater Remediation of Metals, Radionuclides and Nutrients with Permeable Reactive Barriers. [in:] *Handbook of Groundwater Remediation Using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals, and Nutrients*. 1st ed., Naftz D.A., Morrison S.J., Davis J.A., Fuller C.C. Eds., Academic Press, **2002**, Ch. 1; ISBN 9780125135634.

[402] Naftz D.L., Fuller C.C., Davis J.A., Morrison S.J., Rowland R.C., Feltcorn E.M. Field demonstration of three permeable reactive barriers to control uranium contamination in ground water, Fry Canyon, Utah. [in:] *Handbook of Groundwater Remediation Using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals, and Nutrients*. 1st ed., Naftz D.A., Morrison S.J., Davis J.A., Fuller C.C. Eds., Academic Press, **2002**, Ch. 14, pp. 401-434; ISBN 9780125135634.

[403] Morrison S.J., Mushovic P.S., Niesen P.L. Early Breakthrough of Molybdenum and Uranium in a Permeable Reactive Barrier. *Environ. Sci. Technol.* **2006**, *40*: 2018-2024.

[404] Cundy A.B., Hopkinson L., Whitty R.L.D. Use of Iron-based Technologies in Contaminated Land and Groundwater Remediation: A Review. *Sci. Total Environ.* **2008**, *400*: 42-51.

[405] Klimkova S., Cernik M., Lacinova L., Filip J., Jancik D., Zboril R. Zero-Valent Iron Nanoparticles in Treatment of Acid Mine Water from *in situ* Uranium Leaching. *Chemosphere* **2011**, *82*: 1178-1184.

[406] Crane R.A., Dickinson M., Popescu I.C., Scott T.B. Magnetite and Zero-Valent Iron Nanoparticles for the Remediation of Uranium Contaminated Environmental Water. *Water Res.* **2011**, *45*(9): 2931-2942.

[407] Liger E., Charlet L., van Cappellen P. Surface Catalysis of Uranium(VI) Reduction by Iron(II). *Geochim. Cosmochim. Acta* **1999**, *63*: 2939-2955.

[408] Yi Z.J., Xu J.S., Chen M.S., Li W., Yao J., Chen H.L., Wang F. Removal of Uranium(VI) from Aqueous Solution Using Sponge Iron. *J. Radioanal. Nucl. Chem.* **2013**, *298*: 955-961.

[409] Ding C.C., Cheng W.C., Sun B., Wang X.K. Effects of *Bacillus subtilis* on the Reduction of U(VI) by NanoFe(0). *Geochim. Cosmochim. Acta* **2015**, *165*: 86-107.

[410] Chen A., Shang C., Shao J., Zhang J., Huang H. The Application of Iron-based Technologies in Uranium Remediation: A Review. *Sci. Total. Environ.* **2017**, *575*: 1291-1306.

[411] Sunilkumar B., Chkrapani G. Studies on Sorption of Uranium on Chitin: A Solid-State Extractant Application for Removal of Uraniumm from Ground Water. *J. Radioanal. Nucl. Chem.* **2014**, *302*(3): 1489-1493.

[412] Noubactep C., Schoner A., Meinrath G. Mechanism of Uranium(VI) Fixation by Elemental Iron. *J. Hazard. Mater.* **2006**, *132*: 202-212.

[413] O’Hara S., Krug T., Quinn J., Clausen C., Geiger C. Field and Laboratory Evaluation of the Treatment of DNAPL Source Zones Using Emulsified Zero-Valent Iron. *Remediation* **2006**, *16*: 35-56.

[414] Elliott D.W., Zhang W. Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment. *Environ. Sci. Technol.* **2001**, *35*: 4922-4926.

[415] Wachowski L., Domka L. Sources and Effects of Asbestos and Other Mineral Fibres Presence in Ambient Air. *Polish J. Environ. Stud.* **2000**, *9*(6): 443-454.

[416] Wachowski L., Kirszenstejn P. Handling PCB-containing Substances and Waste. [in:] *Waste and Packaging – New Legal Regulations and Obligations*. (in Polish) Urbaniaik W. Ed., Poznań: Ed. Forum Sp. z o.o., **2002**, Ch. 7/2, 6, 1-13.

[417] Wachowski L., Kirszenstejn P. A Review of the Methods for Conversion Waste-containing Halogen Compounds. *Polish J. Environ. Stud.* **2001**, *11*- Suppl. I(6): 13-26.

[418] Fołtynowicz Z., Wachowski L. *Commodity Science and Ecological Aspects of Marketing CFC and HCFC*
Alternatives. (in Polish) Poznań: Ed. Poznań University of Economics and Business, 2009.

[419] Wachowski L., Kirszensztejn P. The Environmental Impact of Freons and Halons. [in:] Education in Advanced Chemistry, Vol. 3, Environmental Chemistry and Protection. Ziółkowski J. Ed., Wrocław: Studio Sense, 1996, 143-166.

[420] Němeček J., Lhots ký O., Cajthaml T. Nanoscale Zero-Valent Iron Application for in situ Reduction of Hexavalent Chromium and Its Effects on Indigenous Microorganism Populations. Sci Total Environ. 2014, 485-486: 739-747.

[421] Reijnders L. Cleaner Nanotechnology and Hazard Reduction of Manufactured Nanoparticles. J. Clean Prod. 2006, 14: 124-133.

[422] Auffan M., Achouak W., Rose J., Roncato M.-A., Chan éac C., Waite D.T., Masion A., Woicik J.C., Wiesner M.R., Bottero J.-Y. Relation Between the Redox State of Iron-Based Nanoparticles and Their Cytotoxicity toward Escherichia coli. Environ. Sci. Technol. 2008, 42(17): 6730-6735.

[423] Wiesner M.R., Lowry G.V., Alvarez P., Dionysiou D., Biswas P. Assessing the Risks of Manufactured Nanomaterials. Environ. Sci. Technol. 2006, 40: 4336-4345.

[424] Chen P.J., Wu W.L., Wu K.C. The Zerovalent Iron Nanoparticle Causes Higher Developmental Toxicity Than Its Oxidation Products in Early Life Stages of Medaka Fish. Water Res. 2013, 47(12): 899-3909.

[425] Keller A.A., Garner K., Miller R.J., Lenihan H.S. Toxicity of Nano-Zero Valent Iron to Freshwater and Marine Organisms. PLoS One 2012, 7(8): e43983.

[426] Kadar E., Rooks P., Lakey C., White D.A. The Effect of Engineered Iron Nanoparticles on Growth and Metabolic Status of Marine Microalgae Cultures. Sci. Total Environ. 2012, 439: 8-17.

[427] El-Temsah Y.S., Joner E.J. Ecotoxicological Effects on Earthworms of Fresh and Aged Nano-Sized Zero-Valent Iron (nZVI) in Soil. Chemosphere 2012, 89(1): 76-82.

[428] Saccà M.L., Fajardo C., Martinez-Gomariz M., Costa G., Nande M., Martin M. Molecular Stress Responses to Nano-Sized Zero-Valent Iron (nZVI) Particles in the Soil Bacterium Pseudomonas stutzeri. PLoS One 2014, 9(2): e2014022.

[429] Saccà M.L., Fajardo C., Costa G., Lobo C., Nande M., Martin M. Integrating Classical and Molecular Approaches to Evaluate the Impact of Nanosized Zero-Valent Iron (nZVI) on Soil Organisms. Chemosphere 2014, 104: 184-189.

[430] Snousy M.G., Zawrah M. Nanoparticles Restrictions in Environmental Cleanup Attachment to Soil Surface Models. Environ. Sci. Technol. 2017, 43: 3803-3808.

[431] Ma X., Gurung A., Deng Y. Phytotoxicity and Uptake of Nanoscale Zero-Valent Iron (nZVI) by Two Plant Species. Sci. Total Environ. 2013, 443: 844-849.

[432] Park K. Toxicity of Nanomaterials and Strategy of Risk Assessment. J. Environ. Toxicol. 2005, 20(4): 259-271.

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