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Materiały Wysokoenergetyczne / High Energy Materials, ***2020****, 12 (1), 37 − 74; DOI 10.22211/matwys/0172E*
ISSN 2083-0165

Review / Przegląd
First published in Polish in 2018.

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, optyczne, 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 powszechne. Proponowane w licznych publikacjach i patentach rozwiązania wskazują na ich uniwersalność, większą efektywność i niższe koszty realizacji procesu rekultywacji w porównaniu z metodami konwencjonalnymi.

Keywords: ZVI nanoparticles, contaminant removal, waste, explosives
Słowa kluczowe: nanocząstki Fe(0), usuwanie zanieczyszczeń, odpady, materiały wybuchowe

Symbols and abbreviations

ACMs Asbestos Containing Materials
BNPs Binary Nanoparticles
CMC Carboxymethyl Cellulose
CVD Chemical Vapour Deposition
DNAPL Dense, Non-aqueous Phase
ENMs Engineered Nano Materials
Fe(0) Zero-valent iron particles
LNAPL Light, Non-aqueous Phase Liquid
m-Fe(0) Zero-valent iron macroparticles
n-Fe(0) Zero-valent iron nanoparticles
n-ZVI Zero-valent Iron nanoparticles
NOM Natural Organic Matter
NPs Nanoparticles
PAA Polyacrylic Acid
PCBs Polychlorinated Biphenyls
PRBs Permeable Reactive Barriers
ROS Reactive Oxygen Species
TCE Tetrachloroethane
WA Nuclear Waste

αFe Particles of alpha iron allotrope
μ-Fe(0) Zero-valent iron microparticles

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. $NaHB_4$, N_2H_4, 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/m^2), 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 processess in an environment, was proposed. This method relies on the measurement of decoloration in a column of methylene blue ($C_{16}H_{18}ClN_3S$), 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_2=CHCl). The latter was observed during the reduction of organohalogen compounds [83-85]. It should be mentioned that **n-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].

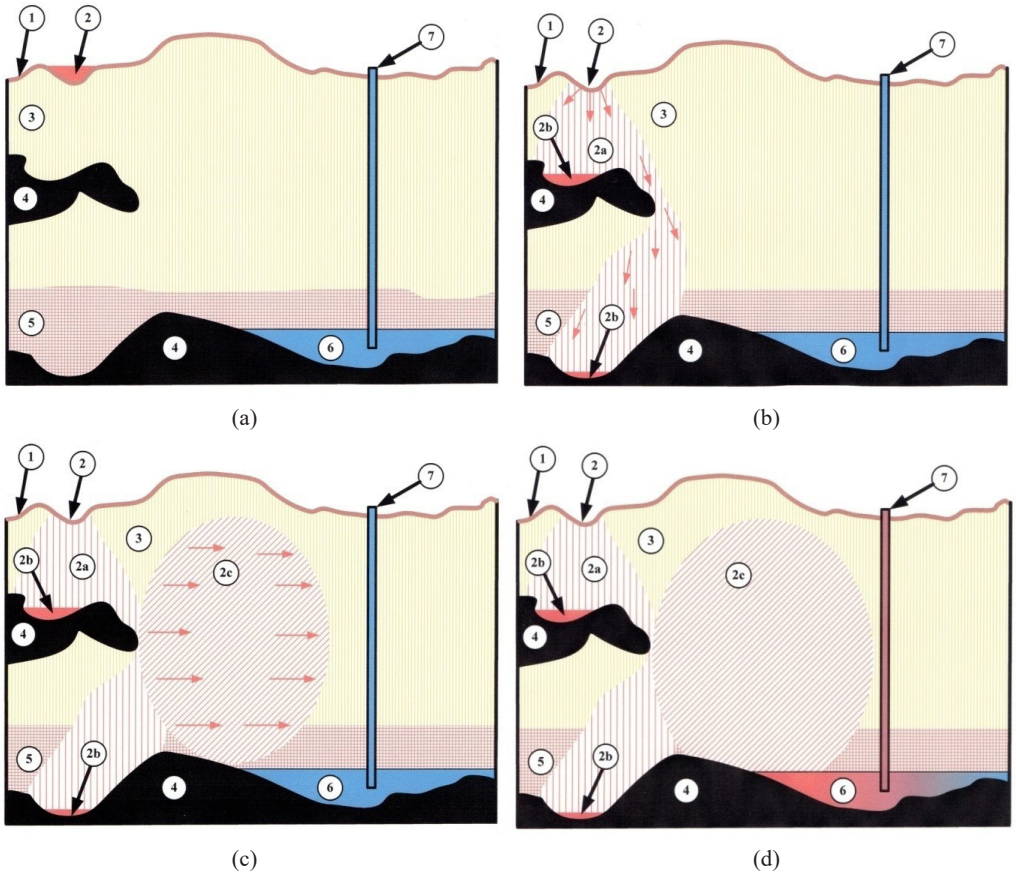


Figure 1. Diagram of the organohalogen contaminant mobility in soil: (a) surface soil contaminants (1 – surface soil layer, 2 – surface contamination area, 3 – permeable bed, 4 – bedrock, 5 – low permeability bed, 6 – groundwater, 7 – water intake), (b) contaminant mobility (2a) and **DNAPL** forming (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

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, *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-) **m-ZVI** > 500,000 nm (500 μm),
b) micro μ**m-ZVI** < 1,000 nm (1 μm),
c) nano **n-ZVI** ≤ 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), Atrittor 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 consistsof reducing the size of material (macro-, micro-) to the nano-scale [1, 19-21, 24, 25, 35, 67, 86]. The synthesis methods are relatively straight forward 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 ($NaBH_4$), potassium borohydride (KBH_4), hydrazine ($N_2H_4 \bullet H_2O$) or ascorbic acid ($C_6H_8O_6$) [1, 7, 15, 17, 19, 23, 26, 30, 34, 90-93]:

$$2Fe^{2+}_{(aq)} + BH^-_{4(aq)} + 3H_2O_{(aq)} \longrightarrow 2Fe^0_{(s)} + H_2BO^-_{3(aq)} + 4H^+_{(aq)} + 2H_{2(g)} \quad (1)$$

$$4Fe^{3+}_{(aq)} + 3BH^-_{4(aq)} + 9H_2O_{(aq)} \longrightarrow 4Fe^0_{(s)} + 3H_2BO^-_{3(aq)} + 12H^+_{(aq)} + 6H_{2(g)} \quad (2)$$

   - geothite [α-FeO(OH)] reduction using dihydrogen (H_2) [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 $\mathbf{M(OR)_n}$, where R-alkyl, referred to as a sol-gel is used to form crystalline and amorphic nano-oxides [21, 35, 95-98]:

$$MOR + H_2O \longrightarrow MOH + ROH \quad (3)$$

$$MOH + ROM \longrightarrow M\text{-}O\text{-}M + ROM \quad (4)$$

   - 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 (KBH_4) and hydrazine ($N_2H_4{\cdot}H_2O$) – 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 ($C_{12}H_{22}O_{11}$), dextrins (complex hydrocarbons), lactic acid ($C_2H_4OHCOOH$), polyphenols and alanines [α-aminoacids –[$CH_3CH(NH_2)COOH$] [90, 92, 103, 108, 113, 114].;

Table 1. Plant materials for extracts and infusions and microorganisms used as Fe(II) and Fe(III) salt reducing agents and **n-ZVI** stabilising agents

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]	
Mulberry (leaves) [35, 90, 92, 108, 110]	
Cherry (leaves) [35, 90, 92, 108, 110]	Viruses [35, 90, 108, 110, 112]
Green tea (leaves) [90, 92, 108, 110, 116, 117]	
Fenugreek (lat. *Trigonella foenum-graecum*) [90, 108-110, 118]	
Sorghum (lat. *Sorghun Moench*) [90, 92, 108, 110, 111, 119]	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)	H_2 reduction	70 nm	Magnetite, (Fe_3O_4)
W.-X. Zhang, Lehigh University, (USA)	$NaBH_4$ 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, O_2, O_3, H_2O_2) and H_2O 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):

$$Fe(0)_{(s)} \longrightarrow Fe(II)_{(aq)} + 2e^-_{(aq)} \tag{5}$$

The main component of the passivating oxide layer is an oxidized Fe(II) layer containing: Fe(II)O, $Fe(III)(OH)_3$, $Fe(II)Fe(III)_2O_4$. The complete oxidation of those products generates geothite [iron(III) hydroxy-hydroxide Fe(III)O(OH)] and iron(III oxy-hydroxide [$Fe_2(III)O_3 \cdot 0.5H_2O$] [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].

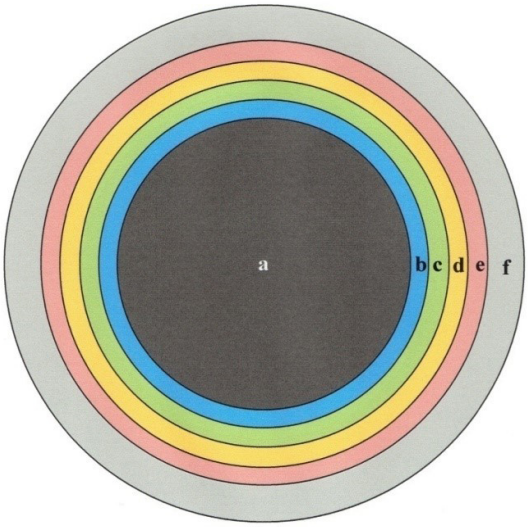
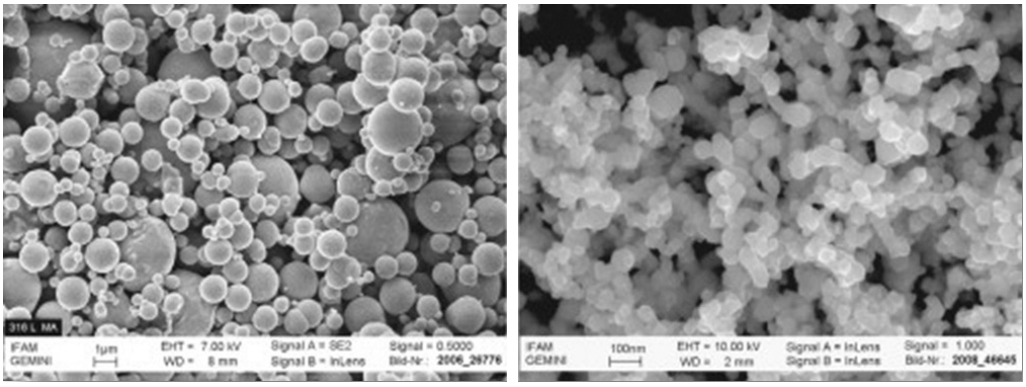


Figure 2. **ZVI** nanoparticles (grains) with the core-shell passivating oxide layer: a) α**ZVI**, b) FeO, c) $Fe(OH)_2$, d) $FeO \cdot Fe_2O_3$, e) FeOOH, f) $Fe_2O_3 \cdot 0.5H_2O$



(a) (b)

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]:

$$5Fe + 7/2O_2 \longrightarrow Fe_2O_3 + Fe_3O_4 \quad (6)$$

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 $(C_6H_{10}O_5)_n$ linear chain, amylose	[158, 159]
	– dextran sulphate	[22, 160]
	– guar gum	[35, 161]
	– alginates, alginic acid calcium or sodium salt	[162]
	– diacetylquinine ($C_{56}H_{103}N_9O_{39}$)	[22, 23, 35, 163-165]
	– cellulose derivative: carboxymethyl cellulose, **CMC**,	[166-169]
	b) chitosan, chitin derivative	[35, 170, 171]
n-Fe_3O_4 ($FeO{\bullet}Fe_2O_3$) (magnetite)	Dipeptide ethyl ester ($C_{14}H_{18}N_2O_5$), 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_2	Mesoporous silica (SiO_2)	[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, amorphic 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_2O 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 **BNPs** [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	NO_3^- 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/SiO_2	Trichlorobenzene dehalogenation	[170]
n-Fe/zeolite	Explosives biodegradation	[235]
Fe/Au	Reduction: NO_3^-	[263, 264]
Fe/Ni	Tetrachloroethane degradation, phenol biodegradation	[256, 257]
Fe/Cu	NO_3^- 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 (O_2) (DO) and to some degree with water, as demonstrated by the following simplified corrosion reactions (Equations 7 and 8) [84, 264, 265]:

$$2Fe(0)_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \longrightarrow 2Fe(II)_{(aq)} + 2H_2O \quad (7)$$

$$Fe(0)(s) + 2H_2O_{(aq)} \longrightarrow Fe(II)_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \quad (8)$$

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):

$$Fe(0)_{(s)} \longrightarrow Fe(II)_{(aq)} + 2e^-_{(aq)} \quad (E0 = -0{,}44\ eV) \quad (9)$$

$$Fe(II)_{(aq)} \longrightarrow Fe(III)_{(aq)} + e^- \quad (E0 = -0{,}77\ eV) \quad (10)$$

$$Fe(0)_{(s)} \longrightarrow Fe(III)_{(aq)} + 3e^{-}_{(aq)} \quad (E0 = -0{,}33\ eV) \tag{11}$$

The corrosion mechanism can also be described as a Heusler mechanism reaction (Equations 12 and 13):

$$Fe(0) + H_2O \longrightarrow (FeOH)_{ads} + H^+ + e^- \tag{12}$$

$$Fe + OH^- \longrightarrow FeOH^+ + 2e^- \tag{13}$$

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

$$(FeOH)_{ads} \longrightarrow FeOH^+ + e^- \tag{14}$$

$$FeOH^+ + H^+ \longrightarrow Fe(II) + H_2O \tag{15}$$

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):

$$Fe(0) \longrightarrow Fe(II) + 2e^- \tag{16}$$

$$2H^+ + 2e^- \longrightarrow 2H^\bullet + 1/2O_2 \longrightarrow H_2O \tag{17}$$

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: $FeO_{0.95}$, $FeO{\cdot}OH$, Fe_2O_3, $[Fe(II)Fe(III)_2O_4]$ [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) beta-elimination, by forming partially dehalogenated short-life intermediate products which in turn are converted into simple hydrocarbons including tetrachloroethene, **TCE**, or ethene (C_2H_4) [268-270],
b) hydrolysis or gradual degradation, where a single chlorine atom is removed at each stage and the final products are simple hydrocarbons, like ethane (C_2H_4), ethane (C_2H_6) *etc.* [83, 97, 103, 271-275], (Equations 18 and 19):

$$RCl + H^+ + 2e^- \longrightarrow RH + Cl^- \tag{18}$$

$$Cl_2C{=}CCl_2 + H^+ + n\text{-}Fe(0) \longrightarrow C_2H_4 + 4Cl^- + Fe(II)/Fe(III) \tag{19}$$

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

$$Fe(0) + Me^{n+} \xrightarrow{e^-} Fe(II) + Me^{(n-x)+} \quad (20)$$

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):

$$Fe(0) + Me^{n+} \xrightarrow{e^-} Fe(II) + Me^{(n-1)+} \xrightarrow{e^-} Fe(II),(III) + Me(0) + e^- \quad (21)$$

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_2O_3) and greigite (Fe_3S_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_3O_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 $\mathbf{Sr^{90}}$ 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.

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

Substance			Ref.
Abbreviation and common name	**Chemical name**	**Chemical formula**	
2-Am-DNT	2-Amino-4,6-dinitrotoluene	$CH_3C_6H_2(NH_2)(NO_2)_2$	[43, 61, 362, 369, 372]
4-Am-DNT	4-Amino-2,6-dinitrotoluene		[43, 61, 362, 369, 373]
CL-20, HNIW	2,4,6,8,10,12-Hexanitrohexaazaisowurtzitane	$C_6N_{12}H_6O_{12}$	[43, 367, 369, 373-375]
DNB	1,3-Dinitrobenzene	$C_6H_4(NO_2)_2$	[43, 61, 362, 369, 372]
DNT	Dinitrotoluenes: 2,4-DNT, 2,6-DNT	$CH_3C_6H_3(NO_2)_2$	[40-43, 49, 360, 361, 366, 372, 376]
EGDN, glycol dinitrate	Ethyl glycol dinitrate	$(CH_2ONO_2)_2$	[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	$C_4H_8N_4(NO_2)_4$	[46, 367, 374, 375, 377]
NC	Nitrocellulose	$[C_6H_9(R_2)_3O_5]_n$	[41-43, 366, 375, 376]
NQ	Nitroguanidine	$(NH_2)CN(NO_2)$	[42, 360, 361, 372, 376, 378]
NTs	2,3,4-Nitrotoluenes	–	[43, 61, 362, 369, 375, 379]
PETN, penthrite	Pentaerythriol tetranitrate	$C[(CH_2ONO_2)]_4$	[43, 362, 369, 372, 373, 375]
PNCBO	1-Chloro-4-nitrobenzene	$ClC_6H_4NO_2$	[43, 269, 362, 369, 375]
RDX, hexogen	1,3,5-Trinitrohexahydro-1,3,5-triazine	$C_3H_6N_3(NO_2)_3$	[40, 46, 47, 61, 309, 369, 377, 380]
TNA	2,4,6-Trinitroanilin	$C_6H_4N_4O_6$	[362, 366, 372, 375, 376]
TNB	1,3,5-Trinitrobenzene	$C_6H_3N_3O_6$	[43, 61, 362, 375, 381]
TNG, TN	1,2,3-Trinitroxypropylene	$C_3H_5(NO_3)_3$	[43, 360, 361, 372, 375, 376]
TNT, trinitrotoluene	2,4,6-Trinitrotoluene	$C_6H_2(NO_2)_3CH_3$	[43, 46, 50, 362, 363, 372, 375-377, 382-387]
Nitramine	2,4,6-Trinitrophenyl-*n*-methylnitramine	$(NO_2)_3C_6H_2N(CH_3)NO_2$	[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 spacial 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 lihtium 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, F, P (white), P (yellow), B, Si,
f) oxides: BaO_2, PbO_2, Pb_3O_4,
g) inorganic compounds: mercury(II) fulminate $Hg(CNO)_2$, lead(II) azide $Pb(N_3)_2$.

Also, a number of monitored toxic organometallic compounds are commonly used, including:
a) tetraethyl lead, $Pb(C_2H_5)_4$,
b) mesoporous chelate polymers, *e.g.* MOF-Fe-ML-101-NH_2,
c) 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:
a) mine effluents [63, 405],
b) contaminated water environment (groundwater) [406-409],
c) 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:
a) 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],
b) good mobility in aporous medium [21, 97, 103, 162, 178, 247, 248, 413],
c) sufficient effective time of action (stability) [28, 57, 89, 176, 178, 187],
d) 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:
a) concentrated aqueous **n-ZVI** suspension (20-30 nm, 255 g/dm^3),
b) emulsifier (6 g/dm^3 xanthan gum biopolymer),
c) 43% H_2O_2,
d) 37.2% vegetable oil,
e) 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 possability 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 magma*, 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.

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Polish version:
The study was originally published in Polish, in the journal *Materiały Wysokoenergetyczne* (*High Energy Materials*) **2018**, *10*: 108-146. This article is available in Polish as a PDF at:
http://www.wydawnictwa.ipo.waw.pl/materialy-wysokoenergetyczne/materialy-wysokoenergetyczne10/HEM_0172.pdf

English version:
– Revised: November 21, 2020
– Published first time online: December 14, 2020