

Applied Environmental Science and Engineering  
for a Sustainable Future

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# Advanced Nano-Bio Technologies for Water and Soil Treatment



Springer

# **Applied Environmental Science and Engineering for a Sustainable Future**

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Editors

# Advanced Nano-Bio Technologies for Water and Soil Treatment

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# Foreword

It is most fitting that this foreword is being written literally on the eve of the very first field-scale demonstration, two decades ago, of the efficacy of nanoscale zero-valent iron (nZVI) as a remediation technology for the treatment of contaminated groundwater at a manufacturing site in Trenton, New Jersey, USA. Memorialized in an *Environ. Sci. Technol.* journal article co-authored with Professor Wei-xian Zhang, the “Father” of the nZVI technology in 2001, this initial work was, in the clarity of retrospection, modest in scope and observations. We found that a kilo of nZVI slurry could be gravity-fed into the surficial sand-dominated aquifer impacted by trichloroethene, that nZVI aggregated very quickly, that the potential for subsurface travel seemed rather limited, and that multiple injections might be required to clean up a site, among others. What we could not have anticipated at that time was the spark this trailblazing work would eventually represent. Since those humble beginnings at Lehigh University, scores of research groups all over the world and some remediation practitioners are working with improved versions of the nZVI technology and a new generation of novel nanomaterials with a common goal—to identify, develop, and apply nanotechnology-based remediation agents to enhance environmental quality, especially that of soils and groundwater which can profoundly impact our potable water supplies. Among the most prolific contributors to this burgeoning community of nanoremediation researchers and practitioners are my colleagues from the Czech Republic who have edited this comprehensive and soon-to-be impactful tome.

The Editors, Principal Investigators, and Subject Matter Experts who contributed to *Advanced Nano-Bio Technologies for Water and Soil Treatment* are among the burgeoning field of applied environmental nanotechnology’s most impactful contributors. Several of these scientists and engineers played key roles in the pivotal EU-led NanoRem consortium of 28 universities, national laboratories, and industry that, from 2013 to 2017, spearheaded the basic research, development, and application of a spectrum of promising nanomaterials for environmental remediation. Over the past 5 years, continued academic interest and, to some degree, the commercial development of key “nanoremediation” technologies are most encouraging. As is

demonstrated throughout the book, nanotechnology has the potential to enhance the performance and effectiveness of traditional remediation remedies by significantly accelerating the rate of contaminant transformation owing to smaller particle sizes. It can expand the spectrum of contaminant classes that can be treated as evidenced in the ability of catalyst-doped nZVI to degrade chlorinated benzenes, whereas iron powders and turnings are largely ineffective. Moreover, the diminution of particle size can enable improved and targeted delivery of remedial agents to subsurface contaminated areas that were previously difficult to reach or inaccessible. Nevertheless, against this largely optimistic backdrop, considerable work remains to fully characterize and appropriately vet the efficacy of these novel nanomaterials, assess the implications of their usage with respect to potential receptors, and conduct robust cost-benefit analyses as many of these technologies lack track records of performance in the field.

Naturally, the book begins with a part (Part I) on reductive technologies, showcasing the standard-bearer nZVI, which now has been showcased in more than 100 field-scale demonstrations around the world. It contrasts the many variations on nZVI with other reducing strategies (e.g., utilization of dithionate) and describes significant new enhancements associated with the application of DC electric fields to help drive nanoremediation agents through low-permeability subsurface formations such as clays. Part II introduces new nano-oxidation technologies, including high valence ferrates, which may provide exciting new water treatment applications. In Part III, the Editors focus on the integration of nanotechnology into the biotreatment of waters and groundwaters. The *ex situ* treatment of soils impacted by persistent organic pollutants such as polycyclic aromatic hydrocarbons using ligninolytic fungi and enzymes is addressed in Part IV. The Editors shift gears with Part V and focus on the implications of using nanoremediation—that is, they address the ecotoxicological impacts on receptors associated with the exposure to nanomaterials in the field. Part VI ties together the overarching observations and conclusions of the spectrum of nano- and nanobiotechnologies covered in the book and forecasts the future prospects of these technologies. Included is discussion on applications for emerging contaminants, new regulatory developments, and how these technologies might fit into new water security and quality strategies. I applaud the Editors, Chapter Authors, and Subject Matter Experts on their contributions and earnestly believe that this book will prove to be an invaluable reference for environmental remediation researchers and practitioners alike.

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10 May 2019

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# Preface

One of the major issues that are currently dealt with all around the world is the depletion of clean/drinking water resources along with losing fertile soil, which would satisfy the burgeoning demand for food supply due to a growing population. Therefore, contamination from industry, environmental accidents, or improper wastewater treatment requires a fast, efficient, and cost-effective action to take. Advanced nanotechnologies, biotechnologies, or their combinations could represent a highly promising ecological and economical alternative to traditional remediation techniques. Due to the diverse character of the target pollutants, the key processes typically involve oxidation, reduction, sorption, and/or biological degradation. In this book, we aim to bridge theory and practice by sharing our experience with eliminating a wide range of pollutants from various resources utilizing innovative nanotechnologies, biotechnologies, and their possible combinations. What has not been omitted is evaluating the toxicity of both emerging pollutants and industrial nanoparticles. All the above-mentioned topics represent the core of an 8-year-long project aimed at applied research entitled “Environmentally friendly nanotechnologies and biotechnologies in water and soil treatment” (NanoBioWat) supported by the Technology Agency of the Czech Republic (project no. TE01020218). The following academic and industrial partners actively participated in the project as well as in the production of this book (all partners are based in the Czech Republic): Palacký University Olomouc, Regional Centre of Advanced Technologies and Materials; Technical University of Liberec, The Institute for Nanomaterials, Advanced Technology and Innovation; Institute of Microbiology of the Czech Academy of Sciences; AECOM CZ s.r.o.; AQUATEST a.s.; DEKONTA, a.s.; GEOTest, a.s.; LAC, s.r.o.; and MEGA, a.s. Leading researchers and experts from the particular fields, being either members of the above-mentioned consortium or based at other institutes, were asked to make their contributions to this book.

This book is organized into five topical parts and covers the most recent findings in the particular fields: (i) *Reductive technologies* for water treatment: this part deals with reductive remedial technologies applicable mainly to an in situ treatment of inorganic and organic contaminants. Nanoscale zero-valent iron is a major reagent



under study, yielding numerous results from various sites under various conditions. Other chemical reductants, such as dithionate, are discussed as well. The enhancement of either natural or chemical processes by DC electric field as a very promising method to accelerate and increase the efficiency of the remedial process along with reducing the cost is tackled as well. (ii) *Oxidative technologies* for water treatment: this part includes a basic overview of various innovative oxidation technologies applicable to water treatment with a strong focus on technologies based on iron compounds in high-valent states (co-called ferrates IV, V, and VI), including the properties of ferrates, their synthesis and applicability. Similarly, radical reactions and photooxidations are covered and discussed regarding their applicability to remediation techniques. (iii) *Biotechnologies for water treatment*: this part provides the overview of modern and advanced methods based on the application of microorganisms and their compartments, especially the combination of microbes or enzymes with nanotechnology applications. A special attention is also paid to recent findings concerning bioelectrical processes participating in the remediation processes. The presented results of nano-bio and bio-nano approaches demonstrate the feasibility and high efficiency of the combined methods. (iv) *Biotechnologies for soil treatment*: this part includes the overview of ex situ bioremediation treatment of contaminated soil. New details about mycoremediation technology using ligninolytic fungi for biodegradation of soil and groundwater contaminated with persistent organic pollutants (POPs) are discussed. The use of a composting technology for polycyclic aromatic hydrocarbons (PAHs) removal from contaminated soil is outlined with respect to its practical application. The last chapter of this part is dedicated to the techniques of bioremediation, including enzymes, biosurfactants, or genetically modified organisms use in real applications. (v) *Ecotoxicology* of both environmental pollutants and nanomaterials used for remediation: this part comprises theoretical support regarding novel findings on ecotoxicity of pollutants and nanomaterials. The importance of this part is underpinned by the fact that there is still lack of a suitable, comprehensive, and standardized set of tests for ecotoxicological evaluation of the novel nanomaterials; further research in this direction is needed.

Each part (i–iv) is organized as follows: it contains chapters focused on general description of the particular technologies followed by several field studies, 10 altogether, demonstrating the applicability of the particular technology. Moreover, the book has a concluding chapter dealing with **future prospects** for techniques treating contaminants of emerging concern in water and soils/sediments. Conclusions and suggestions made not only within this chapter but also throughout the whole book could be of interest to scientists and, primarily, practitioners who deal with water quality. Rising population is a phenomenon that entails different issues ranging from sustainable sources of clean water to cultivating soil for agricultural activities and feeding animals. The last part of the book contains a collection of five **technical chapters** (appendices) providing technical details on actions taken in relation with a pilot/full-scale application of key nano-/biotechnologies. Each chapter focuses on one specific aspect of the implementation of the selected technology/material such as nanoscale zero-valent iron injection into groundwater, field-scale contaminant

monitoring, and nanoparticle migration and transformation. Here we also cover protocols on (eco)toxicological assessment of nanoparticles and evaluation of changes in the microbial communities prior to and after nanoremediation.

Although other previously published papers and books (or book chapters) tackle certain aspects of advanced nano-/biotechnologies, this is the first time a complete and comprehensive treatise on the latest progress in innovative technologies has been published along with clear demonstration of the applicability of the particular methods on the basis of the results yielded in the pilot tests. Therefore, this multidisciplinary book will be suitable for broad readership including environmental scientists, practitioners, policymakers, and toxicologists and, of course, students of diverse fields involving material science, chemistry, biology, geology, hydrogeology, engineering, etc.

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is a named inventor of several European and US patents, e.g., the Development of large-scale technology for the production of zero-valent iron nanoparticles (European patent No. 2164656) or Process of whey protein separation from milk medium and apparatus for its implementation (European patent No. 2873329).

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**Part I**  
**Reductive Technologies**

# Chapter 1

## Geochemical Principles of Reductive Remediation Processes



Miroslav Černík and Josef Zeman

**Abstract** Water is a solvent that is absolutely essential to sustain life. It is one of the world's most precious resources. The uniqueness consists in its polarity, high boiling point, and some other important properties. Several of the water parameters, for example, alkalinity or redox potential, were discussed in this chapter. The environmental significance of these basic parameters is enormous because they are affecting the stability and mobility of substances in the ecosystem, and other parameters are either directly determined or strongly influenced by them. In addition, further important geochemical aspects, presented, for example, in the graphical form, i.e., the  $pE$ - $pH$  diagram (Pourbaix diagram) or redox ladder, were thoroughly explained in this chapter. Subsequently, the in situ chemical reduction (ISCR) techniques were discussed with the special emphasis on the nano zero-valent iron (nZVI). The nZVI reactions and thermodynamics behind them were also reviewed here.

**Keywords** Geochemistry · Redox potential · Nano zero-valent iron (nZVI) · In situ chemical reduction (ISCR)

### 1.1 Introduction

Water is the carrier of the entire geochemical system of natural exogenous processes. Water has a number of unique properties that determine the behavior of the rock matrix and biogenic components. Its basic properties are a high dielectric constant (Malmberg and Maryott 1956), high surface tension, and high heat capacity. Natural water contains dissolved substances, some of which have reduction or oxidation

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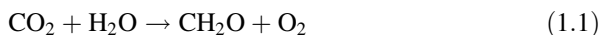
J. Filip et al. (eds.), *Advanced Nano-Bio Technologies for Water and Soil Treatment*, Applied Environmental Science and Engineering for a Sustainable Future, [https://doi.org/10.1007/978-3-030-29840-1\\_1](https://doi.org/10.1007/978-3-030-29840-1_1)

properties. This creates a geochemical balance between the solvent (water), the dissolved substance, and the rock matrix. Altering these conditions also leads to changes in the water chemistry. A significant change in the environment is alkalinity, which in natural waters is mainly a function of the sum of carbonate species and  $\text{OH}^-$ . Therefore, the geochemical system has a certain inertia and, to some degree, can buffer natural oscillations or cause anthropogenically induced changes.

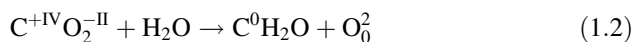
The basic chemical processes used in remediation are mainly changes in acid-alkaline conditions, redox conditions, or the concentration of species causing precipitation. Since the two basic components of chemical reactions are protons and electrons, their exchanges in redox processes and acid-alkaline reactions are fundamental in nature. These processes, which are observed as a reaction of mineral precipitation, weathering, dissolution, or organic matter decomposition, etc., are fundamental reactions occurring on the surface of the earth's crust because of the contact between rock, water, and the atmosphere, and determine the parameters of the surrounding environment. While the significance of pH for the toxicity and mobility of hazardous substances (heavy metals, radionuclides, organic substances, etc.) has been known for a long time, the importance of the redox potential has been significantly underestimated or even neglected except for the oxidation zone of ore deposits. It is commonly assumed that pH is a critical parameter for the state of the natural environment so the other parameters (redox potential, content of dissolved solids in the aqueous environment, concentration of gases) play just a minor role. However, the results of systematic studies on the natural environment and natural processes show that the decisive factors in most cases are redox processes and pH, and the other parameters are either directly determined or strongly influenced by these processes.

## 1.2 Stability of Redox Conditions

The stable redox environment in the geosphere is caused by biota that enables photosynthetic processes. This biota synthesizes complex organic substances from carbon dioxide using solar energy according to the following simplified equation of photosynthesis (Eq. 1.1)



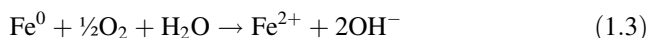
where  $\text{CH}_2\text{O}$  is a general formula for organic matter (like glucose  $\text{C}_6\text{H}_{12}\text{O}_6$ ). During the process, 472 kJ/mol of solar energy is consumed (Stumm and Morgan 1995) and the energy is "stored" and subsequently used to secure the life processes of the biota. When looking at the oxidation state (formal charge, valence) of the substance or compound, reduction of carbon occurs through photosynthesis from oxidation state (+IV) to (0) and an oxidation of oxygen from oxidation state  $-II$  to 0:



Photosynthesis ensures a constant renewal of elemental oxygen, the main oxidant in the geosphere, and produces organic compounds, which enter the soil and water after the biota dies. These organic substances then act as reducing agents through respiration or decay (natural decomposition of organic substances). This process is actually the above-mentioned photosynthetic reaction (Eq. 1.2) in reverse; oxygen is consumed releasing carbon dioxide, water, and energy.

Another very important component of the natural geochemical system is iron. Iron is the most widespread transient metal element and the second most widespread metal on Earth. The content of iron in the Earth's crust is 62 g/kg. In nature, it is mainly found in valence states of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Under oxidation conditions, stable iron is in the valence state of  $\text{Fe}^{3+}$ ; under reducing conditions, it is in the valence state of  $\text{Fe}^{2+}$ , and minerals containing  $\text{Fe}^{3+}$  are also common. Besides oxidation of organic matter, a change in the valence state of Fe is the main process that generates electron transfer in nature. Electrons are generated during oxidation and consumed during reduction.  $\text{Fe}^{4+}$  compounds are very unstable and have no practical significance,  $\text{Fe}^{5+}$  and  $\text{Fe}^{6+}$  compounds are used as very strong oxidizing agents but are not found in nature. Pure iron rarely occurs in nature (in volcanites). Iron in low valence states ( $\text{Fe}^0$ ) can be used as a reducing agent.

In the case of iron (ZVI nanoparticles), it is known that water and dissolved oxygen cause iron oxidation, which leads to corrosion (rusting) by the following Eq. (1.3):



The very name of the redox process—oxidation-reduction reaction—implies that there are two processes occurring—oxidation and reduction, which are inseparable, simultaneous, and dependent. This is a contrast to acid-base reactions, where protons ( $\text{H}^+$  ions) are released by, e.g., acid dissolution in water, solvated and stable in a water environment.

Oxygen participates in the above process in the reduction part in which electrons are consumed and the oxidation state of oxygen reduces according to the formal reaction (Eq. 1.4).



Reversely, iron participates in the oxidation process in which electrons are released and the iron oxidation state increases.



By combining these two equations—reduction (Eq. 1.4) and oxidation (Eq. 1.5) respectively—we obtain the final equation for iron rusting, where two electrons are exchanged between the iron and oxygen. For such a heterogeneous process, the surface area of the solid reagent is the key parameter for the reaction rate. This has a

practical significance only in the case of systems described by a single process because comparison with a more complex process is ambiguous (Tiehm et al. 1997).

### 1.3 Quantitative Expression of Redox Potential

Redox potential is an intensive parameter of the environment and expresses the overall potential of the system for oxidation-reduction processes, just as pH expresses the acidity of acid-base reactions. Usually, the redox potential for a general oxidation-reduction reaction (Stumm and Morgan 1995).



is derived from the well-known Nernst equation (Eq. 1.7).

$$E_h = E_h^\circ + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}} \quad (1.7)$$

where  $E_h$  is the potential of the redox reaction (Eq. 1.6).  $E^\circ$  is the standard potential, i.e., potential in unit activities of oxidized (Ox) and reduced (Red) forms of the substance,  $R$  is the universal gas constant,  $T$  is thermodynamic temperature,  $F$  is Faraday's constant,  $n$  is the number of electrons that are exchanged during the redox reaction between Ox and Red species of the redox pair,  $a_{\text{Ox}}$  and  $a_{\text{Red}}$  are activities of oxidized and reduced species, respectively.

Analogically to pH, which expresses the activity of protons in a solution in the form of a negative decadic logarithm, it is possible to express Eh as the pε, negative decadic logarithm of the activity  $a_{e^-}$  of electrons in the environment:

$$p\varepsilon = -\log a_{e^-} \quad (1.8)$$

with the relation

$$E_h = \frac{2.303RT}{F} p\varepsilon = 0.059 p\varepsilon \quad (1.9)$$

where  $a_{e^-}$  is the activity of electrons.

To measure the potential of electrochemical reactions, it is necessary to use two electrodes between which the potential is measured. One electrode measures the observed response, the other serves as a reference. Platinum is a good material for the electrodes (Schuettler 2007) because it is resistant in most environments and is not subject to its own redox reactions. The reference standard hydrogen electrode (SHE) is a plate coated with spongy black platinum, which is saturated by gaseous hydrogen  $\text{H}_2$  at a pressure of 101.325 kPa and is immersed in a solution with a unit activity of  $\text{H}^+$ .

The electrochemical reaction.



on the reference electrode under standard conditions is arbitrarily given a potential (Eh) of 0 V. For practical reasons, redox potential is measured using other reference electrodes with a stable potential instead of SHE. The most commonly used reference electrodes are Ag/AgCl (silver chloride) (Ives and Janz 1961) and Hg/Hg<sub>2</sub>Cl<sub>2</sub> (calomel) electrodes. Silver chloride electrodes consist of a silver wire coated with AgCl precipitate, which is immersed in a KCl solution with a specific concentration. Based on the KCl concentration in the solution, the potential of the electrode ranges from 197 mV (saturated KCl) to 288.1 mV (0.1 M KCl) and is temperature-dependent. The saturated calomel electrode whose potential is about 247 mV (at 20 °C) works in a similar way. The measured potential must then be recalculated to SHE by adding the above-mentioned values depending on the reference electrode used and the temperature. The values not corrected to SHE are sometimes reported as ORP (oxidation-reduction potential) compared to  $E_h$  or ORP<sub>H</sub> related to SHE.

## 1.4 Stability of Water and Eh-pH Diagrams

The acidity and redox properties of an aqueous environment are the basic parameters affecting the stability and mobility of substances in this environment (Violante et al. 2010). These properties and their influence on the state of a substance can be summarized in the form of Eh-pH (or pE-pH) diagrams. The redox conditions (like pH conditions) of an aqueous environment cannot acquire unlimited values as they are limited by the reaction of water with other substances. Since water in most cases is in contact with the atmosphere (either with the normal atmosphere containing oxygen or with the soil atmosphere containing carbon dioxide or hydrogen), the processes limiting the Eh values are the oxidation or reduction reactions of water producing these gases. Both types of reactions are very similar in principle (Table 1.1). Oxidation can be expressed as a reaction in which water loses the

**Table 1.1** The basic oxidation-reduction reactions of water

Water oxidation	Water reduction
$\text{H}_2\text{O} - 2\text{e}^- \leftrightarrow \frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+$	$\text{H}_2\text{O} + \text{e}^- \leftrightarrow \frac{1}{2}\text{H}_2(\text{g}) + \text{OH}^-$
Equilibrium constant (log form):	Equilibrium constant (log form):
$-\log K = \log a_{\text{H}_2\text{O}} - \frac{1}{2} \log p_{\text{O}_2} + 2\text{pE} + 2\text{pH}$	$\log K = \log K_w + \frac{1}{2} \log p_{\text{H}_2} + \text{pE} + \text{pH}$
pE: Water oxidation	pE: Water reduction
$\text{pE} = 20.78 - \text{pH}$	$\text{pE} = -\text{pH}$

Note,  $p_{\text{O}_2}$  and  $p_{\text{H}_2}$  are the partial pressures of the gases present and  $K_w$  is autoprotolysis constant of water