



**Taking Nanotechnological Remediation Processes
from Lab Scale to End User Applications
for the Restoration of a Clean Environment**

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WP1: Scientific Project Management and Coordination

**DL 1.3 Publication of Scientific Papers:
At least 15 scientific publications from different WP**

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List of editors:

| Name, First Name | Partner Organisation |
|---|--------------------------------|
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Contributions of many NanoRem researchers have been put together for this deliverable.

The authors are separately noted in the included papers.

Executive Summary

NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) is a research project, funded through the European Commission's Seventh Framework Programme. NanoRem focuses on facilitating practical, safe, economic and exploitable nanotechnology for *in-situ* remediation.

As a research project funded by the European Union, NanoRem is obliged to make information about the research progress and the outcomes of the project publically available. Especially with NanoRem's focus on application, it is vital to publish the newly developed and refined technologies to enable others to base their research on work that has already been done.

Therefore, to show the progress made during the project, project partners from all work packages have documented their research and successfully submitted their findings to various international scientific journals, making the research conducted in the NanoRem project available in numerous publications.

NanoRem's goal was to publish at least 15 scientific papers from different work packages during the project. This number has been surpassed, showing the recognition of the project results in the scientific community.

These publications are compiled in this report. It contains abstracts of 22 publications.

Table of Contents

| | |
|--|------------|
| Executive Summary | iii |
| 1.1 <i>List of scientific papers</i> | 1 |
| 2 Abstracts | 5 |
| 2.1 <i>Bardos et al. 2015: 10.1002/rem.21426</i> | 5 |
| 2.2 <i>Bianco et al. 2016: 10.1016/j.jconhyd.2016.08.006</i> | 5 |
| 2.3 <i>Bosch et al. 2014: 10.1007/s00284-014-0539-2</i> | 6 |
| 2.4 <i>Braunschweig et al. 2013: 10.1016/j.nbt.2013.03.008</i> | 6 |
| 2.5 <i>Braunschweig et al. 2014: 10.1016/j.gca.2014.05.006</i> | 7 |
| 2.6 <i>Byrne et al. 2015: 10.1098/rsif.2015.0240</i> | 8 |
| 2.7 <i>Georgi et al. (2015): 10.1016/j.jconhyd.2015.05.002</i> | 8 |
| 2.8 <i>Gillies et al. 2016: 10.1016/j.scitotenv.2016.01.009</i> | 9 |
| 2.9 <i>Hjorth et al. 2016: 10.1002/ieam.1762</i> | 9 |
| 2.10 <i>Hjorth et al. 2017: 10.1039/C6EN00443A</i> | 10 |
| 2.11 <i>Jarošová et al. 2015: 10.1016/j.jenvman.2014.12.007</i> | 10 |
| 2.12 <i>Kumar et al. 2014: 10.1021/es503154q</i> | 11 |
| 2.13 <i>Mackenzie et al. 2015: 10.1016/j.scitotenv.2015.07.107</i> | 12 |
| 2.14 <i>Messina et al. 2015: 10.1016/j.jcis.2015.01.024</i> | 12 |
| 2.15 <i>Muhamadali et al. 2015: 10.1128/AEM.00294-15</i> | 13 |
| 2.16 <i>Ribas et al. 2016: 10.1007/s11051-016-3490-2</i> | 13 |
| 2.17 <i>Schmid et al. 2015: 10.1016/j.jconhyd.2015.01.006</i> | 14 |
| 2.18 <i>Skjolding et al. 2015: 10.1002/anie.201604964</i> | 15 |
| 2.19 <i>Velimirovic 2016: 10.1016/j.scitotenv.2015.11.007</i> | 15 |
| 2.20 <i>Watts et al. 2015: 10.1016/j.apgeochem.2014.12.001</i> | 16 |
| 2.21 <i>Watts et al. 2015: 10.1016/j.apcatb.2015.01.017</i> | 16 |
| 2.22 <i>Watts et al. 2017: 10.1016/j.ibiod.2016.12.008</i> | 17 |

List of Tables

| | |
|---|----------|
| Table 1: Overview of scientific papers | 1 |
|---|----------|

1.1 List of scientific papers

Table 1: Overview of scientific papers

| Title | Journal | Authors | Date | Publisher | Vol/Issue | Pages | DOI | Topics | WP |
|--|----------------------------------|--|----------|--|-----------|----------|-------------------------------|--------|---------|
| Nanoremediation and International Environmental Restoration Markets | Bioremediation Journal | Paul Bardos , Brian Bone, Miroslav Černík, Daniel W. Elliott, Sarah Jones and Corinne Merly | Mar 2015 | Taylor and Francis Inc. | 25(2) | 83-94 | 10.1002/rem.21426 | A | 4, 2, 9 |
| A 3-dimensional micro- and nanoparticle transport and filtration model (MNM3D) applied to the migration of carbon-based nanomaterials in porous media. | Journal of Contaminant Hydrology | Carlo Bianco , Rajandrea Sethi, Tiziana Tosco | Oct 2016 | Elsevier | 193 | 10-20 | 10.1016/j.jconhyd.2016.08.006 | A,D,P | 7 |
| Metabolic Efficiency of <i>Geobacter sulfurreducens</i> Growing on Anodes with Different Redox Potentials | Current Microbiology | Julian Bosch , Keun-Young Lee, Siang-Fu Hong, Falk Harnisch, Uwe Schröder, Rainer U. Meckenstock | Feb 2014 | Springer New York | 68(6) | 763-768 | 10.1007/s00284-014-0539-2 | D, P | 3 |
| Iron oxide nanoparticles in geomicrobiology: from biogeochemistry to bioremediation | New Biotechnology | Braunschweig J, Bosch J, Meckenstock RU | Apr 2013 | Elsevier | 30(6) | 793-802 | 10.1016/j.nbt.2013.03.008 | D, P | 3 |
| Citrate influences microbial Fe hydroxide reduction via a dissolution-disaggregation mechanism | Geochimica et Cosmochimica Acta | Braunschweig , Juliane; Klier, Christine; Schröder, Christian; Händel, Matthias; Bosch, Julian; Totsche, Kai U.; Meckenstock, Rainer U. | Aug 2014 | Elsevier | 139 | 434-446 | 10.1016/j.gca.2014.05.006 | D, P | 3 |
| Scale-up of the production of highly reactive biogenic magnetite nanoparticles using <i>Geobacter sulfurreducens</i> | The Royal Society Interface | J. M. Byrne , H. Muhamadali, V. S. Coker, J. Cooper, J. R. Lloyd | May 2015 | Journal of The Royal Society Interface | 12(107) | 20150240 | 10.1098/rsif.2015.0240 | D | 3 |

| Title | Journal | Authors | Date | Publisher | Vol/Issue | Pages | DOI | Topics | WP |
|--|--|--|----------|----------------------------|-----------|-------------|---------------------------------|--------|---------|
| Colloidal activated carbon for in-situ groundwater remediation - Transport characteristics and adsorption of organic compounds in water-saturated sediment columns | Journal of contaminant hydrology | Georgi A , Schierz A, Mackenzie K, Kopinke FD | Jun 2015 | Elsevier | 179 | 76-88 | 10.1016/j.jconhyd.2015.05.002 | D, P | 2, 3, 4 |
| Fluorescence labelling as tool for zeolite particle tracking in nanoremediation approaches | Science of the Total Environment | Gillies G , Mackenzie K, Kopinke FD, Georgi A | Jun 2016 | Elsevier | 550 | 820-826 | 10.1016/j.scitotenv.2016.01.009 | D, P | 3, 4, 6 |
| The applicability of chemical alternatives assessment for engineered nanomaterials | Integrated Environmental Assessment and Management | Rune Hjorth , Steffen Foss Hansen, Molly Jacobs, Joel Tickner, Michael Ellenbecker and Anders Baun | Apr 2016 | Wiley | 13(1) | 177-187 | 10.1002/ieam.1762 | A | 5 |
| The role of alternative testing strategies in environmental risk assessment of engineered nanomaterials | Environmental Science: Nano | Rune Hjorth , Patricia A. Holden, Steffen Foss Hansen, Benjamin P. Colman, Khara Grieger, Christine Ogilvie Hendren | Jan 2017 | Royal Society of Chemistry | | | 10.1039/C6EN00443A | P | 5 |
| Can zero-valent iron nanoparticles remove waterborne estrogens? | Journal of Environmental Management | Jarošová B , Filip J, Hilscherová K, Tuček J, Šimek Z, Giesy JP, Zbořil R, Bláha L | May 2015 | Academic Press Inc. | 150 | 387-392 | 10.1016/j.jenvman.2014.12.007 | P, A | 2 |
| Molecular Insights of Oxidation Process of Iron Nanoparticles: Spectroscopic, Magnetic and Microscopic Evidences | Environmental Sciences and Technology | Naresh Kumar , Mélanie Auffan, Jérôme Gattacceca, Jérôme Rose, Luca Olivi, Daniel Borschneck, Petr Kvapil, Michael Jublot, Delphine Kaifas, Laure Malleret, Pierre Doumenq, and Jean-Yves Bottero | Nov 2014 | ACS nano | 48(23) | 13888-13894 | 10.1021/es503154q | D, P | 2, 6 |

| Title | Journal | Authors | Date | Publisher | Vol/Issue | Pages | DOI | Topics | WP |
|---|---|---|------------|-----------------------------------|-----------|-------------|---------------------------------|--------|------------|
| Carbo-Iron as improvement of the nanoiron technology: From laboratory design to the field test | Science of the Total Environment | Mackenzie K, Bleyl S, Kopinke FD, Doose H, Bruns J | Aug 2015 | Elsevier | 563-564 | 641-648 | 10.1016/j.scitotenv.2015.07.107 | D,A | 2, 3, 4, 9 |
| An extended and total flux normalized correlation equation for predicting single-collector efficiency | Journal of Colloid and Interface Science | Messina F, Marchisio DL, Sethi R | Jan 2015 | Academic Press Inc. | 446 | 185-193 | 10.1016/j.jcis.2015.01.024 | D, P | 7 |
| Metabolic Profiling of <i>Geobacter sulfurreducens</i> during Industrial Bioprocess Scale-Up | Applied and Environmental Microbiology | Howbeer Muhamadali , Yun Xu, David I. Ellis, J. William Allwood, Nicholas J. W. Rattray, Elon Correa, Haitham Alrabiah, Jonathan R. Lloyd and Royston Goodacre | May 2015 | American Society for Microbiology | 81(10) | 3288-3298 | 10.1128/AEM.00294-15 | D | 3 |
| Improvements in nanoscale zero-valent iron production by milling through the addition of alumina | Journal of Nanoparticle Research | D. Ribas , M. Cernik, V. Martí, J.A. Benito. | Jul 2016 | Springer Link | 18(7) | 181 | 10.1007/s11051-016-3490-2 | D | 2 |
| Measuring the reactivity of commercially available zero-valent iron nanoparticles used for environmental remediation with iopromide | Journal of contaminant hydrology | Schmid D, Micić V, Laumann S, Hofmann T. | Jun 2015 | Elsevier | 181 | 36-45 | 10.1016/j.jconhyd.2015.01.006 | P | 4 |
| Aquatic Ecotoxicity Testing of Nanoparticles-The Quest To Disclose Nanoparticle Effects | Angewandte Chemie - International Edition | Lars Michael Skjolding , Sara Nørgaard Sørensen , Nanna Bloch Hartmann , Rune Hjorth , Steffen Foss Hansen , Anders Baun | Dec 2016 | John Wiley and Sons Ltd | 55(49) | 15224-15239 | 10.1002/anie.201604964 | P | 5 |
| Agar agar-stabilized milled zero-valent iron particles for in situ groundwater remediation | Science of the Total Environment | Velimirovic , M. Schmid D, Wagner S, Micić V, von der Kammer F, Hofmann T. | 18-11-2016 | Elsevier | 563-564 | 713-723 | 10.1016/j.scitotenv.2015.11.007 | P | 4 |

| Title | Journal | Authors | Date | Publisher | Vol/Issue | Pages | DOI | Topics | WP |
|--|---|--|------------|-----------|-----------|---------|---------------------------------|---------|------|
| Biogenic nano-magnetite and nano-zero valent iron treatment of alkaline Cr(VI) leachate and chromite ore processing residue | Applied Geochemistry | Watts , M. P., Coker, V. S., Parry, S. A., Pattrick, R. A. D., Thomas, R. A. P., Kalin, R. & Lloyd, J. R. | 03-2015 | Elsevier | 54 | 27-42 | 10.1016/j.apgeochem.2014.12.001 | P, A | 2, 4 |
| Effective treatment of alkaline Cr(VI) contaminated leachate using a novel Pd-bionanocatalyst; impact of electron donor and aqueous geochemistry | Applied Catalysis B Environmental | Mathew P. Watts , Victoria S. Coker, Stephen A. Parry, Russell A. P. Thomas, Robert Kalin, Jonathan R. Lloyd | 07-2015 | Elsevier | 170-171 | 162-172 | 10.1016/j.apcatb.2015.01.017 | P, A | 3 |
| Highly efficient degradation of organic pollutants using a microbially-synthesized nanocatalyst | International Biodeterioration & Biodegradation | Watts , M.P. Cutting, R.S. Joshi, N., Coker, V.S., Mosberger, A., Zhou, B., Davies, C.M. van Dongen, B.E., Hoffstetter, T. & Lloyd, J.R | 07-01-2017 | Elsevier | | 1-7 | 10.1016/j.ibiod.2016.12.008 | D, P, A | 3 |

Possible topics are:

D = Design and Production; P = Performance in the Environment; A = Application / Stakeholders / Risks / Sustainability

2 Abstracts

2.1 Bardos et al. 2015: 10.1002/rem.21426

Paul Bardos , Brian Bone, Miroslav Černík, Daniel W. Elliott, Sarah Jones and Corinne Merly (2015) Nanoremediation and International Environmental Restoration Markets. *Bioremediation Journal* 25(2), p. 83-94.

Nanoscale zero-valent iron (nZVI) is the most commonly used nanoremediation material. While there has been a reasonable level of application of nZVI technologies for *in situ* remediation in the United States, its utilization across Europe has been much more limited. There has been significant uncertainty about the balance between deployment risks and benefits for nanoparticles (NPs), which has affected the regulatory position in several countries. Some member states of the European Union (EU) take a strong precautionary view of the risks from the deployment of NPs into the subsurface, preventing the adoption of the technology. This article provides a risk–benefit assessment for nZVI based on published information and describes the steps that will be taken by a major European research project (NanoRem), as part of its work to provide a basis for better informed decision making in European environmental restoration markets. A key part of this process is dialogue between practitioners and researchers. NanoRem therefore has an active process of communication with different stakeholder networks (regulators, service providers, and site owners). NanoRem hopes to stimulate a consensus on appropriate use of nanoremediation and thereby stimulate effective technology transfer to the European remediation market. ©2015 The Authors

2.2 Bianco et al. 2016: 10.1016/j.jconhyd.2016.08.006

Carlo Bianco, Rajandrea Sethi, Tiziana Tosco (2016) A 3-dimensional micro- and nanoparticle transport and filtration model (MNM3D) applied to the migration of carbon-based nanomaterials in porous media. *Journal of Contaminant Hydrology* 193, p.10-20.

Engineered nanoparticles (NPs) in the environment can act both as contaminants, when they are unintentionally released, and as remediation agents when injected on purpose at contaminated sites. In this work two carbon-based NPs are considered, namely CARBO-IRON[®], a new material developed for contaminated site remediation, and single layer graphene oxide (SLGO), a potential contaminant of the next future. Understanding and modeling the transport and deposition of such NPs in aquifer systems is a key aspect in both cases, and numerical models capable to simulate NP transport in groundwater in complex 3D scenarios are necessary. To this aim, this work proposes a modeling approach based on modified advection-dispersion-deposition equations accounting for the coupled influence of flow velocity and ionic strength on particle transport. A new modeling tool (MNM3D - Micro and Nanoparticle transport Model in 3D geometries) is presented for the simulation of NPs injection and transport in 3D scenarios. MNM3D is the result of the integration of the numerical code MNMs (Micro and Nanoparticle transport, filtration and clogging Model - Suite) in the well-known transport model RT3D (Clement et al., 1998). The injection in field-like conditions of CARBO-IRON[®] (20 g/l) amended by CMC (4 g/l) in a 2D vertical tank (0.7 × 1.0 × 0.12 m) was simulated using

MNM3D, and compared to experimental results under the same conditions. Column transport tests of SLGO at a concentration (10 mg/l) representative of a possible spill of SLGO-containing waste water were performed at different values of ionic strength (0.1 to 35 mM), evidencing a strong dependence of SLGO transport on IS, and a reversible blocking deposition. The experimental data were fitted using the numerical code MNMs and the ionic strength-dependent transport was up-scaled for a full scale 3D simulation of SLGO release and long-term transport in a heterogeneous aquifer. MNM3D showed to potentially represent a valid tool for the prediction of the long-term behavior of engineered nanoparticles released in the environment (e.g. from landfills), and the preliminary design of in situ aquifer remediation through injection of suspensions of reactive NPs.

2.3 Bosch et al. 2014: 10.1007/s00284-014-0539-2

Julian Bosch, Keun-Young Lee, Siang-Fu Hong, Falk Harnisch, Uwe Schröder, Rainer U. Meckenstock (2015) Metabolic Efficiency of *Geobacter sulfurreducens* Growing on Anodes with Different Redox Potentials. *Current Microbiology* 68(6), p. 763-768.

Microorganisms respiring Fe(III) in the environment face a range of redox potentials of the prospective terminal ferric electron acceptors, because Fe(III) can be present in different minerals or organic complexes. We investigated the adaptation of *Geobacter sulfurreducens* to this range by exposing the bacteria to different redox potentials between the electron donor acetate and solid, extracellular anodes in a microbial fuel-cell set-up. Over a range of anode potentials from -0.105 to $+0.645$ V versus standard hydrogen electrode, *G. sulfurreducens* produced identical amounts of biomass per electron respired. This indicated that the organism cannot utilize higher available energies for energy conservation to ATP, and confirmed recent studies. Either the high potentials cannot be used due to physiological limitations, or *G. sulfurreducens* decreased its metabolic efficiency, and less biomass per unit of energy was produced. In this case, *G. sulfurreducens* “wasted” energy at high-potential differences, most likely as heat to fuel growth kinetics.

2.4 Braunschweig et al. 2013: 10.1016/j.nbt.2013.03.008

Braunschweig J, Bosch J, Meckenstock RU (2013) Iron oxide nanoparticles in geomicrobiology: from bio-geochemistry to bioremediation. *New Biotechnology* 30, p. 793-802.

Iron oxides are important constituents of soils and sediments and microbial iron reduction is considered to be a significant anaerobic respiration process in the subsurface, however low microbial reduction rates of macroparticulate Fe oxides in laboratory studies led to an underestimation of the role of Fe oxides in the global Fe redox cycle. Recent studies show the high potential of nano-sized Fe oxides in the environment as, for example, electron acceptor for microbial respiration, electron shuttle between different microorganisms, and scavenger for heavy metals. Biotic and abiotic reactivity of iron macroparticles differ significantly from nano-sized Fe oxides, which are usually much more reactive. Factors such as particle size, solubility, ferrous iron, crystal structure, and organic molecules were identified to influence the reactivity. This review discusses factors influencing the microbial reactivity of Fe oxides. It highlights the differences between natural and synthetic Fe oxides especial-

ly regarding the presence of organic molecules such as humic acids and natural organic matter. Attention is given to the transport behavior of Fe oxides in laboratory systems and in the environment, because of the high affinity of different contaminants to Fe oxide surfaces and associated co-transport of pollutants. The high reactivity of Fe oxides and their potential as adsorbents for different pollutants are discussed with respect to application and development of remediation technologies.

2.5 Braunschweig et al. 2014: 10.1016/j.gca.2014.05.006

Braunschweig, Juliane; Klier, Christine; Schröder, Christian; Händel, Matthias; Bosch, Julian; Totsche, Kai U.; Meckenstock, Rainer U. (2014) Citrate influences microbial Fe hydroxide reduction via a dissolution-disaggregation mechanism. *Geochimica et Cosmochimica Acta* 139, p. 434-446.

Microbial reduction of ferric iron is partly dependent on Fe hydroxide particle size: nanosized Fe hydroxides greatly exceed the bioavailability of their counterparts larger than 1 μm . Citrate as a low molecular weight organic acid can likewise stabilize colloidal suspensions against aggregation by electrostatic repulsion but also increase Fe bioavailability by enhancing Fe hydroxide solubility. The aim of this study was to see whether adsorption of citrate onto surfaces of large ferrihydrite aggregates results in the formation of a stable colloidal suspension by electrostatic repulsion and how this effect influences microbial Fe reduction. Furthermore, we wanted to discriminate between citrate-mediated colloid stabilization out of larger aggregates and ferrihydrite dissolution and their influence on microbial Fe hydroxide reduction. Dissolution kinetics of ferrihydrite aggregates induced by different concentrations of citrate and humic acids were compared to microbial reduction kinetics with *Geobacter sulfurreducens*. Dynamic light scattering results showed the formation of a stable colloidal suspension and colloids with hydrodynamic diameters of 69 (± 37) to 165 (± 65) nm for molar citrate:Fe ratios of 0.1 to 0.5 and partial dissolution of ferrihydrite at citrate:Fe ratios ≥ 0.1 . No dissolution or colloid stabilization was detected in the presence of humic acids. Adsorption of citrate, necessary for dissolution, reversed the surface charge and led to electrostatic repulsion between sub-aggregates of ferrihydrite and colloid stabilization when the citrate:Fe ratio was above a critical value (≤ 0.1). Lower ratios resulted in stronger ferrihydrite aggregation instead of formation of a stable colloidal suspension, owing to neutralization of the positive surface charge. At the same time, microbial ferrihydrite reduction increased from 0.029 to 0.184 mM h^{-1} indicating that colloids stabilized by citrate addition enhanced microbial Fe reduction.

Modelling of abiotic dissolution kinetics revealed that colloid stabilization was most pronounced at citrate:Fe ratios of 0.1 - 0.5, whereas higher ratios led to enhanced dissolution of both colloidal and larger aggregated fractions. Mathematical simulation of the microbial reduction kinetics under consideration of partial dissolution and colloid stabilization showed that the bioaccessibility increases in the order large aggregates < stable colloids < Fe-citrate.

These findings indicate that much of the organic acid driven mobilization of Fe oxy(hydr)oxides is most likely due to colloid formation and stabilization rather than solubilisation.

2.6 Byrne et al. 2015: 10.1098/rsif.2015.0240

J. M. Byrne, H. Muhamadali, V. S. Coker, J. Cooper, J. R. Lloyd (2015) Scale-up of the production of highly reactive biogenic magnetite nanoparticles using *Geobacter sulfurreducens*. *Journal of The Royal Society Interface* 12(107), p. 20150240.

Although there are numerous examples of large-scale commercial microbial synthesis routes for organic bioproducts, few studies have addressed the obvious potential for microbial systems to produce inorganic functional biomaterials at scale. Here we address this by focusing on the production of nanoscale biomagnetite particles by the Fe(III)-reducing bacterium *Geobacter sulfurreducens*, which was scaled up successfully from laboratory- to pilot plant-scale production, while maintaining the surface reactivity and magnetic properties which make this material well suited to commercial exploitation. At the largest scale tested, the bacterium was grown in a 50 l bioreactor, harvested and then inoculated into a buffer solution containing Fe(III)-oxyhydroxide and an electron donor and mediator, which promoted the formation of magnetite in under 24 h. This procedure was capable of producing up to 120 g of biomagnetite. The particle size distribution was maintained between 10 and 15 nm during scale-up of this second step from 10 ml to 10 l, with conserved magnetic properties and surface reactivity; the latter demonstrated by the reduction of Cr(VI). The process presented provides an environmentally benign route to magnetite production and serves as an alternative to harsher synthetic techniques, with the clear potential to be used to produce kilogram to tonne quantities.

2.7 Georgi et al. (2015): 10.1016/j.jconhyd.2015.05.002

Georgi A, Schierz A, Mackenzie K, Kopinke FD (2015) Colloidal activated carbon for in-situ groundwater remediation - Transport characteristics and adsorption of organic compounds in water-saturated sediment columns. *Journal of contaminant hydrology* 179, p. 76-88.

Colloidal activated carbon can be considered as a versatile adsorbent and carrier material for in-situ groundwater remediation. In analogy to other nanoremediation approaches, activated carbon colloids (ACC) can be injected into the subsurface as aqueous suspensions. Deposition of ACC on the sediment creates a sorption barrier against further spreading of hydrophobic pollutants. This study deals with the optimization of ACC and their suspensions with a focus on suspension stability, ACC mobility in saturated porous media and sorption efficiency towards organic contaminants. ACC with an appropriate particle size range ($d_{50}=0.8\mu\text{m}$) were obtained from a commercial powdered activated carbon product by means of wet-grinding. Among the various methods tested for stabilization of ACC suspensions, addition of humic acid (HA) and carboxymethyl cellulose (CMC) showed the best results. Due to electrosteric stabilization by adsorption of CMC, suspensions remained stable even at high ACC concentrations (11gL^{-1}) and conditions typical of very hard water (5mM divalent cations). Furthermore, CMC-stabilized ACC showed high mobility in a water-saturated sandy sediment column (filter coefficient $\lambda=0.2\text{m}^{-1}$). Such mobility is a pre-requisite for in-situ installation of sorption or reaction barriers by simple injection-well or direct-push application of ACC suspensions. Column experiments with organic model compounds proved the efficacy of ACC deposits on sediment for contaminant adsorption and retardation under flow-through conditions.

2.8 Gillies et al. 2016: 10.1016/j.scitotenv.2016.01.009

Gillies G, Mackenzie K, Kopinke FD, Georgi A (2016) Fluorescence labelling as tool for zeolite particle tracking in nanoremediation approaches. *Science of the Total Environment* 550, p. 820-826.

Colloidal Fe-zeolites such as Fe-BEA-35 are currently under study as new adsorbent and catalyst materials for in-situ chemical oxidation with H₂O₂. As for nanoremediation in general, the availability of suitable particle detection methods is a requirement for successful process development and particle tracing. Detection and distinguishing between natural colloids and introduced particles with a similar composition are a challenge. By means of fluorescence labelling, a highly specific detection option for Fe-BEA-35 was developed. 'Ship-in-a-bottle' synthesis of fluorescein within the zeolite pores, which was applied for the first time for a BEA type zeolite, provides a product with stable and non-extractable fluorescence. When the fluorescent labelled zeolite is added at a concentration of 1wt.% referring to the total zeolite mass, a very low detection limit of 1mg/L of total zeolite is obtained. Compared to commonly applied turbidity measurements, detection via fluorescence labelling is much more specific and sensitive. Fluorescence is only marginally affected by carboxymethyl cellulose, which is frequently applied as stabilizer in application suspensions but will be depleted upon contact with H₂O₂. Transport properties of fluorescent labelled and non-labelled Fe-zeolite particles are in agreement as determined in a column study with quartz sand and synthetic groundwater (classified as very hard).

2.9 Hjorth et al. 2016: 10.1002/ieam.1762

Rune Hjorth, Steffen Foss Hansen, Molly Jacobs, Joel Tickner, Michael Ellenbecker and Anders Baun (2016) The applicability of chemical alternatives assessment for engineered nanomaterials. *Integrated Environmental Assessment and Management*, Vol 13, Issue 1 p. 177-187.

The use of alternatives assessment to substitute hazardous chemicals with inherently safer options is gaining momentum worldwide as a legislative and corporate strategy to minimize consumer, occupational, and environmental risks. Engineered nanomaterials represent an interesting case for alternatives assessment approaches, because they can be considered both emerging "chemicals" of concern, as well as potentially safer alternatives to hazardous chemicals. However, comparing the hazards of nanomaterials to traditional chemicals or to other nanomaterials is challenging, and critical elements in chemical hazard and exposure assessment may have to be fundamentally altered to sufficiently address nanomaterials. The aim of this paper is to assess the overall applicability of alternatives assessment methods for nanomaterials and to outline recommendations to enhance their use in this context. The present paper focuses on the adaptability of existing hazard and exposure assessment approaches to engineered nanomaterials as well as strategies to design inherently safer nanomaterials. We argue that alternatives assessment for nanomaterials is complicated by the sheer number of nanomaterials possible. As a result, the inclusion of new data tools that can efficiently and effectively evaluate nanomaterials as substitutes is needed to strengthen the alternatives assessment process. However, we conclude that with additional tools to enhance traditional hazard and

exposure assessment modules of alternatives assessment, such as the use of mechanistic toxicity screens and control banding tools, alternatives assessment can be adapted to evaluate engineered nanomaterials as potential substitutes for chemicals of concern and to ensure safer nanomaterials are incorporated in the design of new products.

2.10 Hjorth et al. 2017: 10.1039/C6EN00443A

Rune Hjorth, Patricia A. Holden, Steffen Foss Hansen, Benjamin P. Colman, Khara Grieger, Chris-tine Ogilvie Hendren (2017) The role of alternative testing strategies in environmental risk assessment of engineered nanomaterials. *Environmental Science: Nano*

Within toxicology there is a pressure to find new test systems and organisms to replace, reduce and refine animal testing. In nanoecotoxicology the need for alternative testing strategies (ATS) is further emphasized as the validity of tests and risk assessment practices developed for dissolved chemicals are challenged. Nonetheless, standardized whole organism animal testing is still considered the gold standard for environmental risk assessment. Advancing risk analysis of engineered nanomaterials (ENMs) through ATS was discussed in September 2014 at an international Society for Risk Analysis (SRA) workshop in Washington, D.C. and serves as the point of departure for this paper. Here we present the main outcomes by describing and defining the use of ATS for ENMs as well as discussing its future role in environmental risk science. We conclude that diversity in testing should be encouraged to avoid “selective ignorance” and that, through an iterative process with low-tier and high-tier testing, data-generation can be validated to ensure relevant endpoints. Furthermore, simplified screening of ENMs could enable early decision-making on material design, while complex multi-species studies should be utilized to skip uncertain environmental extrapolations and give rise to more accurate risk analysis.

2.11 Jarošová et al. 2015: 10.1016/j.jenvman.2014.12.007

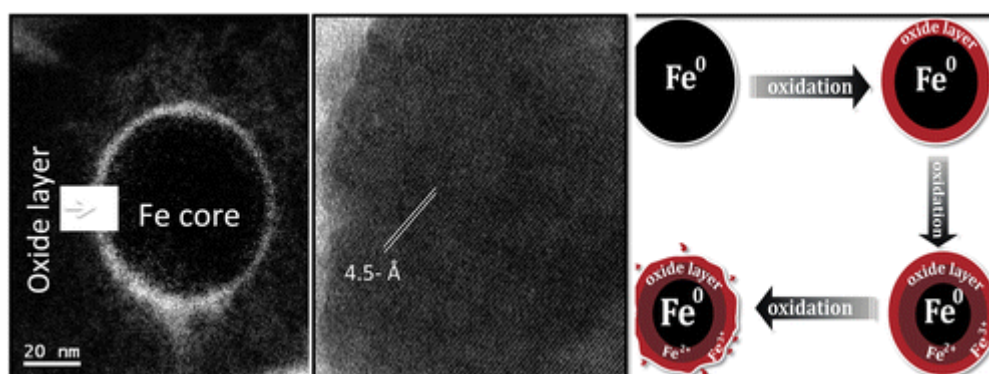
Jarošová B, Filip J, Hilscherová K, Tuček J, Šimek Z, Giesy JP, Zbořil R, Bláha L (2015) Can zero-valent iron nanoparticles remove water-borne estrogens? *Journal of Environmental Management* 150, p. 387-392.

Steroidal estrogens are one of the most challenging classes of hazardous contaminants as they can cause adverse effects to biota in extremely low concentrations. They emerge in both waste waters and surface waters serving as a source of drinking water. Environmental Quality Standards for 17 β -estradiol (E2) and 17 α -ethinylestradiol (EE2), promulgated within the EU Water Framework Directive, are 0.4 and 0.035 ng L⁻¹, respectively. Because nanoscale zero-valent iron (nZVI) particles have been previously used in numerous remediation technologies and have the advantage of possible magnetic separation, interaction of nZVI with E2 and EE2 in water was investigated to assess the potential role of nZVI in removing steroidal estrogens. A mixture of E2 and EE2 dissolved in water was shaken with varying doses of nZVI for 1-5 h. Concentration-dependent removal of the estrogens was observed but removal did not increase significantly with time. Concentrations of the estrogens were determined by HPLC/MS/MS and a biodetection reporter gene assay. Sorption and nonspecific

oxygen-mediated oxidation of estrogens were identified as the most probable removal mechanisms. Two independent experiments confirmed that significant decrease of estrogens concentration is achieved when at least 2 g L⁻¹ of nZVI is applied. The presented study provides insights into the mechanisms of nZVI interaction with steroidal estrogens under aerobic conditions prevailing in currently applied water treatment technologies.

2.12 Kumar et al. 2014: 10.1021/es503154q

Naresh Kumar, Mélanie Auffan, Jérôme Gattacceca, Jérôme Rose, Luca Olivi, Daniel Borschneck, Petr Kvapil, Michael Jublot, Delphine Kaifas, Laure Mal-leret, Pierre Dou-menq, and Jean-Yves Bottero (2014) Molecular insights of oxidation process of iron nano-particles: spectroscopic, magnetic and microscopic evidences. *Environmental Sciences and Technology* 48(23), p. 13888-13894.



Oxidation behavior of nano-Fe⁰ particles in an anoxic environment was determined using different state-of-the-art analytical approaches, including high resolution transmission electron microscopy (HR-TEM) combined with energy filtered transmission electron microscopy (EFTEM), X-ray absorption spectroscopy (XAS), and magnetic measurements. Oxidation in controlled experiments was compared in standard double distilled (DD) water, DD water spiked with trichloroethene (TCE), and TCE contaminated site water. Using HR-TEM and EFTEM, we observed a surface oxide layer (~3 nm) formed immediately after the particles were exposed to water. XAS analysis followed the dynamic change in total metallic iron concentration and iron oxide concentration for the experimental duration of 35 days. The metallic iron concentration in nano-Fe⁰ particles exposed to water, was ~40% after 35 days; in contrast, the samples containing TCE were reduced to ~15% and even to nil in the case of TCE contaminated site water, suggesting that the contaminants enhance the oxidation of nano-Fe⁰. Frequency dependence measurements confirmed the formation of superparamagnetic particles in the system. Overall, our results suggest that nano-Fe⁰ oxidized via the Fe⁰ – Fe(OH)₂ – Fe₃O₄ – (γ-Fe₂O₃) route and the formation of superparamagnetic maghemite nanoparticles due to disruption of the surface oxide layer.

2.13 Mackenzie et al. 2015: 10.1016/j.scitotenv.2015.07.107

Mackenzie K, Bleyl S, Kopinke FD, Doo-se H, Bruns J (2015) Carbo-Iron as improvement of the nanoiron technology: From laboratory design to the field test. *Science of the Total Environment* 563-564, p. 641-648.

In a first pilot-scale field test the use of Carbo-Iron® was successfully demonstrated. Carbo-Iron was developed with the goal to overcome significant shortcomings of nanoscale zero-valent iron (NZVI) for in-situ groundwater remediation. The composite material of colloidal activated carbon and embedded nanoiron structures has been tested for the remediation of a tetrachloroethene (PCE) contaminated field site in Lower Saxony, Germany. The results of the two-step field test confirmed the properties intended by its design and the particle performance achieved in the laboratory experiments. The material showed transport lengths of several metres in the field and fast PCE decomposition with no vinyl chloride formation. Extended longevity of the PCE decrease in the treated area and evidence for microbiological participation were found. Carbo-Iron is now under study in the framework of the EU-project NanoREM where its performance is being further optimized at various scales from laboratory via large-scale tank to field testing. Targeted property adjustment was successful for Carbo-Iron performance in both directions: plume treatment and source attack.

2.14 Messina et al. 2015: 10.1016/j.jcis.2015.01.024

Messina F, Marchisio DL, Sethi R (2015) An extended and total flux normalized correlation equation for predicting single-collector efficiency. *Journal of Colloid and Interface Science* 446, p. 185-193.

In this study a novel total flux normalized correlation equation is proposed for predicting single-collector efficiency under a broad range of parameters. The correlation equation does not exploit the additivity approach introduced by Yao et al. (1971), but includes mixed terms that account for the mutual interaction of concomitant transport mechanisms (i.e., advection, gravity and Brownian motion) and of finite size of the particles (steric effect). The correlation equation is based on a combination of Eulerian and Lagrangian simulations performed, under Smoluchowski-Levich conditions, in a geometry which consists of a sphere enveloped by a cylindrical control volume. The normalization of the deposited flux is performed accounting for all of the particles entering into the control volume through all transport mechanisms (not just the upstream convective flux as conventionally done) to provide efficiency values lower than one over a wide range of parameters. In order to guarantee the independence of each term, the correlation equation is derived through a rigorous hierarchical parameter estimation process, accounting for single and mutual interacting transport mechanisms. The correlation equation, valid both for point and finite-size particles, is extended to include porosity dependency and it is compared with previous models. Reduced forms are proposed by elimination of the less relevant terms.

2.15 Muhamadali et al. 2015: 10.1128/AEM.00294-15

Howbeer Muhamadali, Yun Xu, David I. Ellis, J. William Allwood, Nicholas J. W. Rattray, Elon Correa, Haitham Alrabiah, Jona-than R. Lloyd and Royston Goodacre (2015) Metabolic Profiling of *Geobacter sulfurreducens* during Industrial Bioprocess Scale-Up. *Applied and Environmental Microbiology* 81(10), p. 3288-3298.

During the industrial scale-up of bioprocesses it is important to establish that the biological system has not changed significantly when moving from small laboratory-scale shake flasks or culturing bottles to an industrially relevant production level. Therefore, during upscaling of biomass production for a range of metal transformations, including the production of biogenic magnetite nanoparticles by *Geobacter sulfurreducens*, from 100-ml bench-scale to 5-liter fermentors, we applied Fourier transform infrared (FTIR) spectroscopy as a metabolic fingerprinting approach followed by the analysis of bacterial cell extracts by gas chromatography-mass spectrometry (GC-MS) for metabolic profiling. FTIR results clearly differentiated between the phenotypic changes associated with different growth phases as well as the two culturing conditions. Furthermore, the clustering patterns displayed by multivariate analysis were in agreement with the turbidimetric measurements, which displayed an extended lag phase for cells grown in a 5-liter bioreactor (24 h) compared to those grown in 100-ml serum bottles (6 h). GC-MS analysis of the cell extracts demonstrated an overall accumulation of fumarate during the lag phase under both culturing conditions, coinciding with the detected concentrations of oxaloacetate, pyruvate, nicotinamide, and glycerol-3-phosphate being at their lowest levels compared to other growth phases. These metabolites were overlaid onto a metabolic network of *G. sulfurreducens*, and taking into account the levels of these metabolites throughout the fermentation process, the limited availability of oxaloacetate and nicotinamide would seem to be the main metabolic bottleneck resulting from this scale-up process. Additional metabolite-feeding experiments were carried out to validate the above hypothesis. Nicotinamide supplementation (1 mM) did not display any significant effects on the lag phase of *G. sulfurreducens* cells grown in the 100-ml serum bottles. However, it significantly improved the growth behavior of cells grown in the 5-liter bioreactor by reducing the lag phase from 24 h to 6 h, while providing higher yield than in the 100-ml serum bottles.

2.16 Ribas et al. 2016: 10.1007/s11051-016-3490-2

D. Ribas, M. Cernik, V. Martí, J.A. Benito (2016) Improvements in nanoscale zero-valent iron production by milling through the addition of alumina. *Journal of Nanoparticle Research* 18(7), p. 18:181.

A new milling procedure for a cost-effective production of nanoscale zero-valent iron for environmental remediation is presented. Conventional ball milling of iron in an organic solvent as Mono Ethylene Glycol produces flattened iron particles that are unlikely to break even after very long milling times. With the aim of breaking down these iron flakes, in this new procedure, further milling is carried out by adding an amount of fine alumina powder to the previously milled solution. As the amount of added alumina increases from 9 to 54 g l⁻¹, a progressive decrease of the presence of flakes is observed. In the latter case, the appearance of the particles formed by fragments of former

flakes is rather homogeneous, with most of the final nanoparticles having an equivalent diameter well below 1 μm and with an average particle size in solution of around 400 nm. An additional increase of alumina content results in a highly viscous solution showing worse particle size distribution. Milled particles, in the case of alumina concentrations of 54 g l⁻¹, have a fairly large specific surface area and high Fe(0) content. These new particles show a very good Cr(VI) removal efficiency compared with other commercial products available. This good reactivity is related to the absence of an oxide layer, the large amount of superficial irregularities generated by the repetitive fracture process during milling and the presence of a fine nanostructure within the iron nanoparticles.

2.17 Schmid et al. 2015: 10.1016/j.jconhyd.2015.01.006

Schmid D, Micić V, Laumann S, Hofmann T. (2015) Measuring the reactivity of commercially available zero-valent iron nanoparticles used for environmental remediation with iopromide. *Journal of contaminant hydrology* 181, p. 36-45.

The high specific surface area and high reactivity of nanoscale zero-valent iron (nZVI) particles have led to much research on their application to environmental remediation. The reactivity of nZVI is affected by both the water chemistry and the properties of the particular type of nZVI particle used. We have investigated the reactivity of three types of commercially available Nanofer particles (from Nanoiron, s.r.o., Czech Republic) that are currently either used in, or proposed for use in full scale environmental remediation projects. The performance of one of these, the air-stable and thus easy-to-handle Nanofer Star particle, has not previously been reported. Experiments were carried out first in batch shaking reactors in order to derive maximum reactivity rates and provide a rapid estimate of the Nanofer particle's reactivity. The experiments were performed under near-natural environmental conditions with respect to the pH value of water and solute concentrations, and results were compared with those obtained using synthetic water. Thereafter, the polyelectrolyte-coated Nanofer 25S particles (having the highest potential for transport within porous media) were chosen for the experiments in column reactors, in order to elucidate nanoparticle reactivity under a more field-site realistic setting. Iopromide was rapidly dehalogenated by the investigated nZVI particles, following pseudo-first-order reaction kinetics that was independent of the experimental conditions. The specific surface area normalized reaction rate constant (kSA) value in the batch reactors ranged between 0.12 and 0.53 Lm⁻²h⁻¹; it was highest for the uncoated Nanofer 25 particles, followed by the polyacrylic acid-coated Nanofer 25S and air-stable Nanofer Star particles. In the batch reactors all particles were less reactive in natural water than in synthetic water. The kSA values derived from the column reactor experiments were about 1000 times lower than those from the batch reactors, ranging between 2.6×10⁻⁴ and 5.7×10⁻⁴ Lm⁻²h⁻¹. Our results revealed that the easy-to-handle and air-stable Nanofer Star particles are the least reactive of all the Nanofer products tested. The reaction kinetics predicted by column experiments were more realistic than those predicted by batch experiments and these should therefore be used when designing a full-scale field application of nanomaterials for environmental remediation.

2.18 Skjolding et al. 2015: 10.1002/anie.201604964

Lars Michael Skjolding, Sara Nørgaard Sørensen, Nanna Bloch Hartmann, Rune Hjorth, Steffen Foss Hansen, Anders Baun (2016) Aquatic Ecotoxicity Testing of Nanoparticles—The Quest To Disclose Nanoparticle Effects *Angewandte Chemie - International Edition* Vol 55, Issue 49, p. 15224-15239.

The number of products on the market containing engineered nanoparticles (ENPs) has increased significantly, and concerns have been raised regarding their ecotoxicological effects. Environmental safety assessments as well as relevant and reliable ecotoxicological data are required for the safe and sustainable use of ENPs. Although the number of publications on the ecotoxicological effects and uptake of ENPs is rapidly expanding, the applicability of the reported data for hazard assessment is questionable. A major knowledge gap is whether nanoparticle effects occur when test organisms are exposed to ENPs in aquatic test systems. Filling this gap is not straightforward, because of the broad range of ENPs and the different behavior of ENPs compared to “ordinary” (dissolved) chemicals in the ecotoxicity test systems. The risk of generating false negatives, and false positives, in the currently used tests is high, and in most cases difficult to assess. This Review outlines some of the pitfalls in the aquatic toxicity testing of ENPs which may lead to misinterpretation of test results. Response types are also proposed to reveal potential nanoparticle effects in the aquatic test organisms.

2.19 Velimirovic 2016: 10.1016/j.scitotenv.2015.11.007

Velimirovic, M. Schmid D, Wagner S, Micić V, von der Kammer F, Hofmann T. (2016) Agar agar-stabilized milled zerovalent iron particles for in situ groundwater remediation. *Science of the Total Environment* 563-564, p. 713-723.

Submicron-scale milled zerovalent iron (milled ZVI) particles produced by grinding macroscopic raw materials could provide a cost-effective alternative to nanoscale zerovalent iron (nZVI) particles for in situ degradation of chlorinated aliphatic hydrocarbons in groundwater. However, the aggregation and settling of bare milled ZVI particles from suspension presents a significant obstacle to their in situ application for groundwater remediation. In our investigations we reduced the rapid aggregation and settling rate of bare milled ZVI particles from suspension by stabilization with a “green” agar agar polymer. The transport potential of stabilized milled ZVI particle suspensions in a diverse array of natural heterogeneous porous media was evaluated in a series of well-controlled laboratory column experiments. The impact of agar agar on trichloroethene (TCE) removal by milled ZVI particles was assessed in laboratory-scale batch reactors. The use of agar agar significantly enhanced the transport of milled ZVI particles in all of the investigated porous media. Reactivity tests showed that the agar agar-stabilized milled ZVI particles were reactive towards TCE, but that their reactivity was an order of magnitude less than that of bare, non-stabilized milled ZVI particles. Our results suggest that milled ZVI particles could be used as an alternative to nZVI particles as their potential for emplacement into contaminated zone, their reactivity, and expected longevity are beneficial for in situ groundwater remediation.

2.20 Watts et al. 2015: 10.1016/j.apgeochem.2014.12.001

Watts, M. P., Coker, V. S., Parry, S. A., Pattrick, R. A. D., Thomas, R. A. P., Kalin, R. & Lloyd, J. R. (2015) Biogenic nano-magnetite and nano-zero valent iron treatment of alkaline Cr(VI) leachate and chromite ore processing residue. *Applied Geochemistry* 54, p. 27-42.

Highly reactive nano-scale biogenic magnetite (BnM), synthesized by the Fe(III)-reducing bacterium *Geobacter sulfurreducens*, was tested for the potential to remediate alkaline Cr(VI) contaminated waters associated with chromite ore processing residue (COPR). The performance of this biomaterial, targeting aqueous Cr(VI) removal, was compared to a synthetic alternative, nano-scale zero valent iron (nZVI). Samples of highly contaminated alkaline groundwater and COPR solid waste were obtained from a contaminated site in Glasgow, UK. During batch reactivity tests, Cr(VI) removal from groundwater was inhibited by ~25% (BnM) and ~50% (nZVI) when compared to the treatment of less chemically complex model pH 12 Cr(VI) solutions. In both the model Cr(VI) solutions and contaminated groundwater experiments the surface of the nanoparticles became passivated, preventing complete coupling of their available electrons to Cr(VI) reduction. To investigate this process, the surfaces of the reacted samples were analyzed by TEM-EDX, XAS and XPS, confirming Cr(VI) reduction to the less soluble Cr(III) on the nanoparticle surface. In groundwater reacted samples the presence of Ca, Si and S was also noted on the surface of the nanoparticles, and is likely responsible for earlier onset of passivation. Treatment of the solid COPR material in contact with water, by addition of increasing weight% of the nanoparticles, resulted in a decrease in aqueous Cr(VI) concentrations to below detection limits, via the addition of $\geq 5\%$ w/w BnM or $\geq 1\%$ w/w nZVI. XANES analysis of the Cr K-edge, showed that the % Cr(VI) in the COPR dropped from 26% to a minimum of 4-7% by the addition of 5% w/w BnM or 2% w/w nZVI, with higher additions unable to reduce the remaining Cr(VI). The treated materials exhibited minimal re-mobilization of soluble Cr(VI) by re-equilibration with atmospheric oxygen, with the bulk of the Cr remaining in the solid fraction. Both nanoparticles exhibited a considerable capacity for the remediation of COPR related Cr(VI) contamination, with the synthetic nZVI demonstrating greater reactivity than the BnM. However, the biosynthesized BnM was also capable of significant Cr(VI) reduction and demonstrated a greater efficiency for the coupling of its electrons towards Cr(VI) reduction than the nZVI.

2.21 Watts et al. 2015: 10.1016/j.apcatb.2015.01.017

Mathew P. Watts, Victoria S. Coker, Stephen A. Parry, Russell A. P. Thomas, Robert Kalin, Jonathan R. Lloyd (2015) Effective treatment of alkaline Cr(VI) contaminated leachate using a novel Pd-bionanocatalyst; impact of electron donor and aqueous geochemistry. *Applied Catalysis B Environmental* 170-171, p. 162-172.

Palladium catalysts offer the potential for the effective treatment of a variety of priority reducible pollutants in natural waters. In this study, microbially synthesized magnetite nanoparticles were functionalized with Pd(0), creating a highly reactive, magnetically recoverable, nano-scale catalyst (Pd-BnM). This was then investigated for the treatment of model Cr(VI) contaminated solutions at a range of pH values, and also alkaline Cr(VI) contaminated leachates from chromite ore processing residue (COPR); a contaminant issue of global concern. The sample of COPR used in this study was

obtained from a site in Glasgow, UK, where extensive Cr(VI) contamination has been reported. In initial experiments Pd-BnM was supplied with H₂ gas or formate as electron donors, and Cr(VI) removal from model synthetic solutions was quantified at various pH values (2–12). Effective removal was noted at neutral to environmentally relevant alkaline (pH 12) pH values, while the use of formate as an electron donor resulted in loss of performance under acidic conditions (pH 2). Reaction kinetics were then assessed with increasing Pd-BnM loading in both model pH 12 Cr(VI) solutions and the COPR leachate. When formate was used as the electron donor for Pd-BnM, to treat COPR leachate, there was significant inhibition of Cr(VI) removal. In contrast, a promotion of reaction rate, was observed when H₂ was employed. Upon sustained reaction with model Cr(VI) solutions, in the presence of excess electron donor (formate or H₂), appreciable quantities of Cr(VI) were removed before eventual inactivation of the catalyst. Faster onset of inactivation was reported in the COPR leachates, removing 4% and 64% of Cr(VI) observed from model Cr(VI) solutions, when formate and H₂ were used as electron donors, respectively. XAS, TEM-EDX and XPS analysis of the catalysts that had been inactivated in the model solution, showed that the surface had an extensive covering of reduced Cr(III), most likely as a CrOOH phase. COPR reacted catalysts recorded a lower abundance of Cr(III) alongside a high abundance of the leachate components Ca and Si, implicating these elements in the faster onset of inactivation.

2.22 Watts et al. 2017: 10.1016/j.ibiod.2016.12.008

Watts, M.P. Cutting, R.S. Joshi, N., Coker, V.S., Mosberger, A., Zhou, B., Davies, C.M. van Dongen, B.E., Hoffstetter, T. & Lloyd, J.R (2017) Highly efficient degradation of organic pollutants using a microbially-synthesized nanocatalyst. *International Biodeterioration & Biodegradation* 1, p. 1-7.

Magnetite is a common subsurface mineral, formed biogenically in anaerobic environments. Containing Fe(II), it is reactive towards a variety of common redox sensitive subsurface contaminants. To extend the reactivity of biomagnetite it is possible to add a coating of Pd(0) nanostructures, which is capable of sustained catalytic reactivity. Here we assess the reactivity of biogenic nano-magnetite (BnM), formed by the reduction of Fe(III) oxyhydroxide by *Geobacter sulfurreducens*, to the model organic compounds nitrobenzene (ArNO₂) and tetrachloroethylene (PCE), and compare its performance to biomagnetite functionalized with Pd(0) (Pd-BnM). The BnM and the Pd-BnM were both found to be highly reactive towards ArNO₂, quantitatively transforming it to the reduced product aniline (ArNH₂). When applied to tetrachloroethylene (PCE), the BnM was found to be poorly reactive, while the Pd-BnM rapidly dechlorinated the PCE to the benign product, ethane, at rates comparable to synthetic nano-scale catalysts. The biological synthesis route proposed is highly scalable and offers a green, environmentally benign route for the production of highly reactive nanoparticles for environmental clean-up.