The use of different zero-valent iron nanoparticles for the remediation of effluent water from a small biological wastewater treatment plant

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**Introduction**

Nanomaterials, including **nanoscale zero-valent iron (nZVI) particles**, known by their distinctive chemical, physical, catalytic, and electronic properties, are being intensively investigated for the remediation of contaminated wastewaters, soils, and sediments.

**Aims**

![Image of nanomaterials and processes](image)

**Degradation of organic matter**

- $\text{Me-Fe-OOH}$
- $\text{Me}^{2+}$
- $\text{Me}^{+}$
- $\text{Me}^{0}$

**Processes**

- Co-precipitation
- Reduction
- Adsorption
- Membrane disruption
- Adhesion
- Inclusion
- Protein oxidation
- DNA damage
- Lipid peroxidation
SAMPLING

SBWTP: biological (biodegradation of soluble organic impurities) and mechanical treatment, nitrification, release of cleaned water into surface waters
COD<150 mg O₂/L
BOD<30 mg O₂/L

Sampling was performed at SBWTP Hruševo (100 PU), 18 times, covering all four seasons
Concentration of selected organic parameters in outflow of waste water from small biological water treatment plants (SBWTP) in Slovenia

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Concentration</th>
<th>Limit value for drinking water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed organic bound halogens</td>
<td>mg/L Cl</td>
<td>0,028</td>
<td></td>
</tr>
<tr>
<td>Volatile halogenated halocarbons</td>
<td>mg/L Cl</td>
<td>&lt;0,003</td>
<td></td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>mg/L</td>
<td>&lt;0,00004</td>
<td></td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>mg/L</td>
<td>&lt;0,0007</td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>mg/L</td>
<td>&lt;0,0004</td>
<td>0,003</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>mg/L</td>
<td>&lt;0,0001</td>
<td></td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>mg/L</td>
<td>&lt;0,0001</td>
<td></td>
</tr>
<tr>
<td>Tetrachloroetene</td>
<td>mg/L</td>
<td>&lt;0,0002</td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>mg/L</td>
<td>&lt;0,001</td>
<td></td>
</tr>
<tr>
<td>Sum - organochlorine pesticides</td>
<td>mg/L</td>
<td>&lt;0,01</td>
<td></td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>mg/L</td>
<td>&lt;0,00001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Hexachlorocyclohexane</td>
<td>mg/L</td>
<td>&lt;0,0001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Lindane</td>
<td>mg/L</td>
<td>&lt;0,0001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Endosulfan (sum alfa and beta endosulfan and endosulfan sulphate)</td>
<td>mg/L</td>
<td>&lt;0,0001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Aldrin</td>
<td>mg/L</td>
<td>&lt;0,00001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>mg/L</td>
<td>&lt;0,00001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Endrin</td>
<td>mg/L</td>
<td>&lt;0,00001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>mg/L</td>
<td>&lt;0,00001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Heptachlor epoxide cis</td>
<td>mg/L</td>
<td>&lt;0,00001</td>
<td>0,0001</td>
</tr>
<tr>
<td>Isodrin</td>
<td>mg/L</td>
<td>&lt;0,00001</td>
<td>0,0001</td>
</tr>
</tbody>
</table>

Organic pollutants determined in the effluent water from SBWTP, were below the maximal permitted values for drinking water.
Experimental design

In house nZVI

\[ 2\text{FeCl}_3 + 6\text{NaBH}_4 + 18\text{H}_2\text{O} \rightarrow 2\text{Fe}^0 + 6\text{NaCl} + 6\text{B(OH)}_3 + 21\text{H}_2 \]

Engineered nZVI Nanofer STAR and Nanofer Slurry25
air-stable powder of nZVI stabilized by inorganic stabilizers

Effluent water from SBWTP

Treatment with different FeNPs

Without treatment

In house nZVI

Nanofer STAR

Nanofer25 slurry

Optimization of iron load (0.1 - 5 g L\(^{-1}\)), mixing (30 - 1200 min), at 180 or 1200 min settling time

Analyses

Escherichia coli
Intestinal enterococci
Clostridium perfringens
Coliform bacteria

TN\(_b\), NH\(_4\)\(^+\), NO\(_2\)-, NO\(_3\)-, Al, As, B, Cd, Cr, Cu, Fe, Hg, Mn, Na, Ni, Pb, Sb, Se, Zn
Characteristics of nZVI investigated

<table>
<thead>
<tr>
<th>Parameter</th>
<th>In house nZVI</th>
<th>Nanofer STAR</th>
<th>Nanofer25 slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (nm)</td>
<td>30 - 100</td>
<td>30 - 80</td>
<td>20 - 80</td>
</tr>
<tr>
<td>Shell thickness (nm)</td>
<td>4 - 6</td>
<td>5 - 8</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>disordered</td>
<td>crystalline</td>
<td>crystalline</td>
</tr>
<tr>
<td>BET (m² g⁻¹)</td>
<td>83.0 ± 4.1</td>
<td>17.0 ± 0.8</td>
<td>44.0 ± 2.2</td>
</tr>
<tr>
<td>Available Fe⁰ (wt. %)</td>
<td>88.0 ± 4.4</td>
<td>69.0 ± 3.4</td>
<td>85.0 ± 4.2</td>
</tr>
<tr>
<td>Hydrophobicity (Kₐₒₗₖ)</td>
<td>0.0954</td>
<td>0.0212</td>
<td>0.0956</td>
</tr>
</tbody>
</table>

Field-Emission Scanning Electron Microscopy (FESEM) and Transmission electron microscopy (TEM) images, and Selected area electron diffraction (SAED) patterns

(A) in house nZVI
(B) Nanofer STAR
(C) Nanofer25 slurry
Mean pH values of effluent water samples (n=18) from the SBWTP, and the influence of increasing iron loads from the in house nZVI, Nanofer STAR, and Nanofer25 slurry (mixing time: 60 min, settling time: 1200 min) on the pH of the remediated effluent water samples (n=3).
The influence of increasing iron loads from the in house nZVI (A), Nanofer STAR (B) and Nanofer25 slurry (C) (mixing time 60 min; settling time 1200 min) on the concentration of elements determined in remediated water samples from the SBWTP. The data represent the mean values obtained from three experiments.
The influence of increasing iron loads from the in house nZVI (A), Nanofer STAR (B) and Nanofer25 slurry (C) (mixing time 60 min; settling time 1200 min) on the concentration of N species determined in remediated water samples from the SBWTP. The data represent the mean values obtained from three experiments.

**Constituents of organic N in wastewater from households:**
- **Urea:** $\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3$
  - $\text{NH}_3$ is soluble in water, yielding $\text{NH}_4^+$
- **Proteins (degradation to amino acids and ammonium by nZVI)**
The experimentally obtained MPN and CFU ranges for the bacteria determined in the effluent water samples (n=18) from the SBWTP.
The influence of increasing iron loads from the in house nZVI (A), Nanofer STAR (B) and Nanofer25 slurry (C) (mixing time 60 min; settling time 1200 min) on the disinfection efficiency \((C_x/C_i)\) of effluent water from the SBWTP. The data represent the mean values obtained from three experiments.

\(C_i\) = MPN or CFU before remediation

\(C_x\) = MPN or CFU after remediation
The influence of increasing iron loads from the Nanofer25 slurry (mixing time 240 min; settling time 1200 min) on the disinfection efficiency \((C_x/C_i)\) of effluent water from the SBWTP. The data represent the mean values obtained from three experiments.

\(C_i\) = MPN or CFU before remediation
\(C_x\) = MPN or CFU after remediation
The influence of increasing mixing time (at a constant settling time of 180 min) on the disinfection efficiency \((C_x/C_i)\) of the effluent water from the SBWTP by Nanofer25 slurry (iron load 0.5 g L\(^{-1}\)). The data represent the mean values obtained from three experiments.

\(C_i\) = MPN or CFU before remediation

\(C_x\) = MPN or CFU after remediation
Investigation of the nZVI behaviour after their use in nanoremediation by single particle ICP-MS

Single particle ICP-MS

- determination of particle mass/number concentration of metal-based NPs
- determination of the size and size distribution of metal-based NPs
- low detection limits (<ng/mL)
- simultaneous quantification of analyte in nanosized and dissolved form

QQQ-ICP-MS instrumental parameters for single particle analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction gas flow rate</td>
<td>5.0 mL min⁻¹ H₂ in MS/MS mode</td>
</tr>
<tr>
<td>Sample uptake flow rate</td>
<td>0.300 - 0.330 mL min⁻¹</td>
</tr>
<tr>
<td>Data acquisition mode</td>
<td>Time resolved analysis</td>
</tr>
<tr>
<td>Integration time per isotope</td>
<td>3 ms</td>
</tr>
<tr>
<td>Total acquisition time</td>
<td>60 s - 180 s</td>
</tr>
<tr>
<td>Isotope monitored</td>
<td>⁵⁶Fe</td>
</tr>
</tbody>
</table>

Efficient removal of polyatomic interferences (⁴⁰Ar₁₆O⁺ and ⁴⁰Ca₁₆O⁺) for measurement of ⁵⁶Fe

Sensitive and interference-free measurement of nZVI by SP-ICP-MS
Investigation of the nZVI behaviour after their use in nanoremediation by single particle ICP-MS

After 5 days of settling 99.0% of Fe in the nanoscale form (particles of 43 nm) and 99.5% of Fe present in particles in sizes below 36 nm is removed.

The influence of settling time on the mass concentration of Fe in nanoscale form in effluent water from SBWTP, treated with 0.25 g/L iron load.

The use of nZVI for nanoremediation does not represent environmental threat due to their rapid aggregation and settling.
CONCLUSIONS

- The reactivity of the nZVI had an important influence on their efficiency of disinfection, and governed the amount of ammonium N formed in the remediated effluent water.

- The amount of ammonium N species generated from organic N, and the formation of ammonium cation by the reduction of nitrates and nitrites after the treatment of the effluent water with FeNPs, depends strongly on the reactivity of the investigated nZVI and on the pH of the remediated water.

- The Nanofer25 slurry most effectively removed potentially toxic elements and inactivated pathogenic bacteria at a low \(0.5 \text{ g L}^{-1}\) iron load. At optimal mixing and settling times almost 100% disinfection efficiency was achieved.

- The results demonstrated that the use of nZVI is environmentally safe. Nanoparticles rapidly aggregate and settle and do not represent a nano-threat.

- Additional cleaning steps need to be applied to obtain water of adequate quality which would fulfill the requirements for the drinking water.
Acknowledgements

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