Aquifer modification: an approach to improve the mobility of nZVI used for *in situ* groundwater remediation

Department of Environmental Geosciences

universität wien

Doris SCHMID, Vesna MICIĆ, Milica VELIMIROVIĆ, Stephan WAGNER, Frank von der KAMMER & Thilo HOFMANN

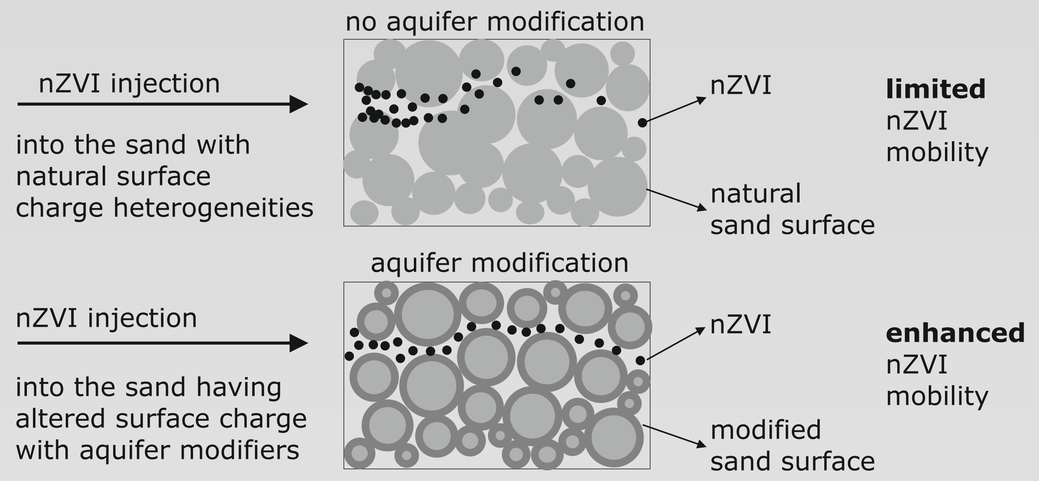
BACKGROUND

Limited mobility of nanoscale zero-valent iron (nZVI) remains an obstacle for the nZVI-based groundwater remediation.

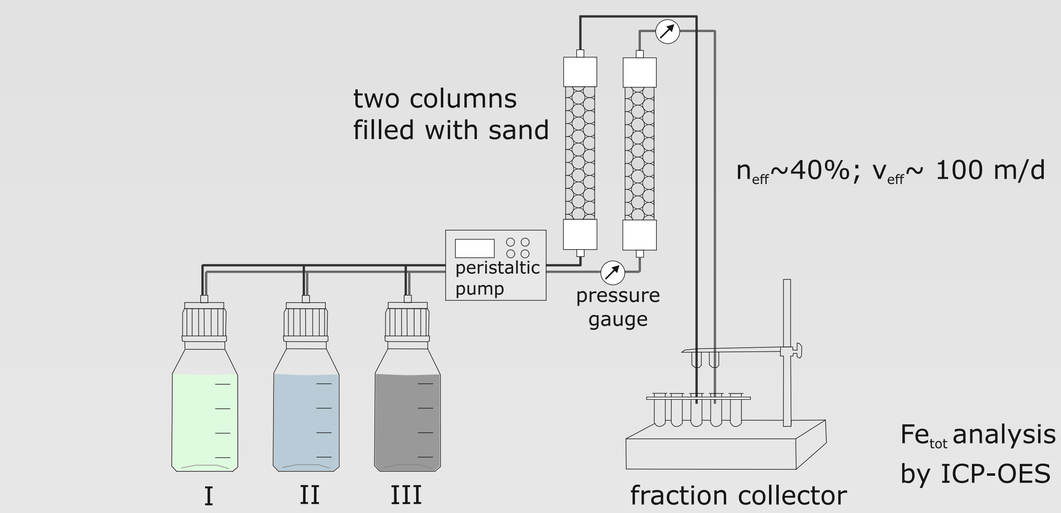
Beside straining and sedimentation, also attachment to positively charged ”patches” on the **mineral grain surfaces hinders the mobility of nZVI**.

Hypothesis: An increase in mobility of nZVI may be achieved by increasing the negative surface charge of the mineral grain surfaces (modifying aquifers) via pre-injection of inexpensive polyelectrolytes into sand.

THE CONCEPT OF AQUIFER MODIFICATION



EXPERIMENTAL SETUP



MATERIALS

SAND

Chemical composition [%]: SiO_2: 98.5; Al_2O_3: 0.47; Fe_2O_3: 0.18; CaO: 0.02; MgO: 0.01; Na_2O: 0.02; K_2O: 0.07; TiO_2: 0.11; P_2O_5: 0.01.
Grain size [mm]: d_{10}: 0.36; d_{50}: 0.65; d_{90}: 0.88.
Mineralogy [%]: quartz: 96; feldspar: 2; kaolinite:1.

WATER

1. MQ (electrolyte-free) water (Millipore, Elix®5-Milli-Q® Gradient A10). Electrical conductivity: 0.054 µS/cm at 25°C.

2. EPA (electrolyte-rich) water (U.S. EPA moderately hard standard water)[mg/L]: $[Na^+]$:26.8; $[K^+]$:2.3; $[Ca^{2+}]$:13.8;$[Mg^{2+}]$:11.2;$[Cl^-]$:2.2;$[SO_4^{2-}]$:79.3;$[NO_3^-]$:0.6; $[HCO_3^-]$:67.3; Electrical conductivity: 297 µS/cm at 22.6°C.

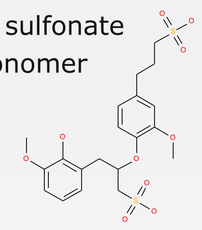
nZVI

Nanofer 25S suspension (polyacrylic acid coated-nZVI, Nanoiron, s.r.o., CZ).
Particle concentration: 1 g/L.

AQUIFER MODIFIERS

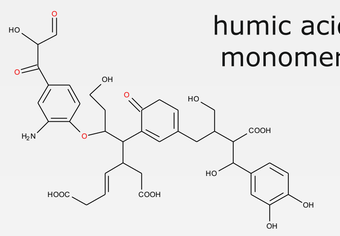
1. Water-soluble sodium lignin sulfonate (Otto Dille® Baeck GmbH & Co. KG, DE).
2. Water-soluble sodium humate (Humintech® GmbH, DE).

lignin sulfonate monomer



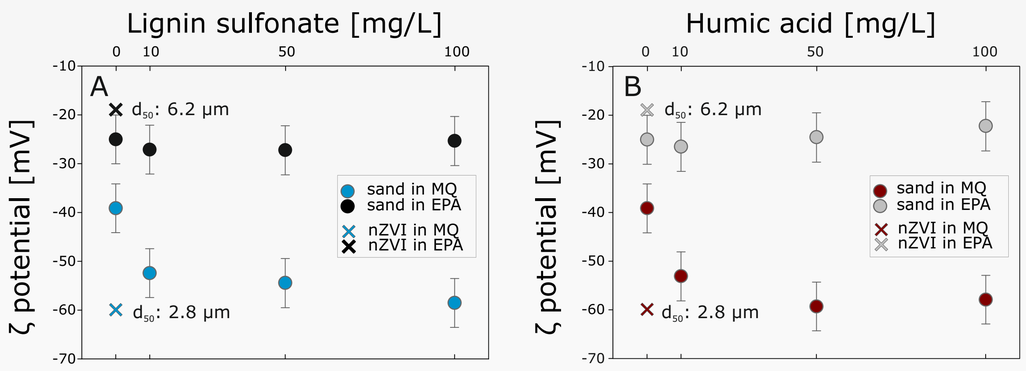
Tentative structure of lignin sulfonate monomer
Source: http://www.chemicalregister.com

humic acid monomer



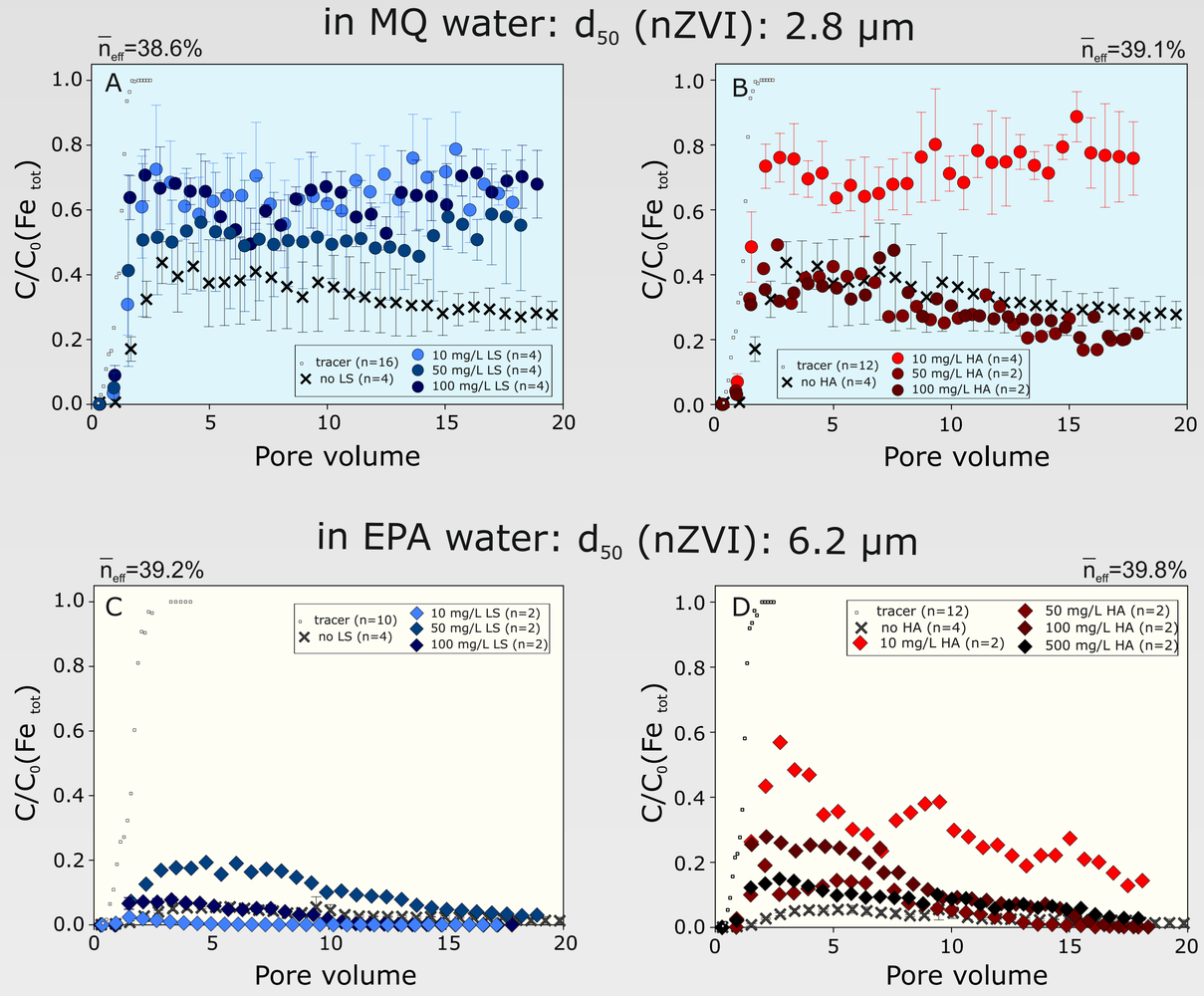
Tentative structure of humic acid monomer
Source: doi:10.1039/b001869o

CHARACTERIZATION OF MATERIALS



Zeta (ζ) potential of nZVI (calculated from the electrophoretic mobility) and **of sand** (calculated from the streaming potential) measured in a sand column modified with **lignin sulfonate (A) and humic acid (B) solutions in MQ and in EPA water.** Note that the ζ potential of both sand and nZVI is significantly lower in MQ than in EPA water and that the nZVI aggregates are larger in EPA than in MQ water.

RESULTS



Mean breakthrough curves of nZVI (measured as Fe_{tot}) **before and after injection of different solutions of aquifer modifiers.** n is number of replicates. Error bars show standard deviation for n>3.

(A) Modification of sand surfaces with lignin sulfonate (LS) solutions in electrolyte–free (MQ) water increases the mobility of nZVI independent on LS concentrations. (B) Only after aquifer modification with 10 mg/L of humic acid (HA) solution in MQ water the mobility of nZVI was improved.

In electrolyte-rich (EPA) water is nZVI practically immobile. (C) Aquifer modification with LS solutions in EPA water does not improve mobility of nZVI. (D) Only after aquifer modification with 10 mg/L of HA solution in EPA water mobility of nZVI was improved.

CONCLUSIONS

- The **ζ potential of sand decreased** when its surface was modified **with** the solution of **modifiers prepared in MQ** water, but not in EPA water.
- The two types of modifiers have different effects on the nZVI transport depending on the type of water.
  - Aquifer modification with different concentrations of lignin sulfonate (LS) in MQ water shows a potential to increase mobility of nZVI with the Fe_{tot} breakthrough varying between 0.5 and 0.7. Conversely, modifying the aquifer with LS solution in EPA water shows no effect on nZVI mobility with the Fe_{tot} breakthrough remaining <0.2.
  - Aquifer modification with a 10 mg/L humic acid solution in both MQ and EPA waters enhances mobility of nZVI, while the higher concentrations show no effect on mobility of nZVI.
- Further work will be dedicated to better understanding the mechanisms behind these observations.

This research receives funding from the European Union's Seventh Framework Programme FP7/2007-2013 under grant agreement n°309517.

NanoRem