Can sodium humate coating on mineral surfaces hinder the deposition of nZVI?

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INTRODUCTION and AIM

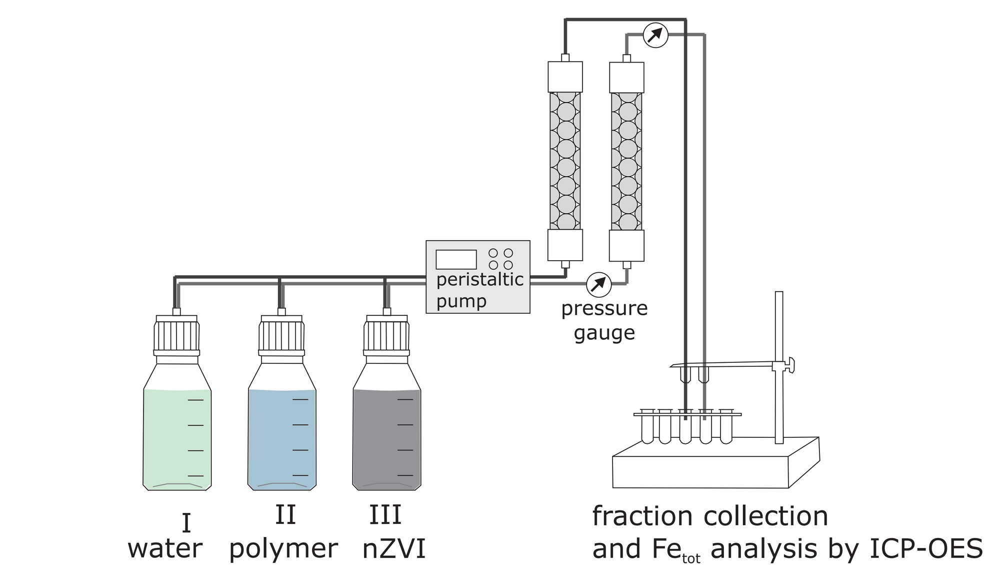
The affinity between nano scale zero valent iron (**nZVI**) **and mineral surfaces hinders** the mobility of nZVI injected into contaminated aquifers and thus **the effectiveness of the remediation technology as a whole**.

nZVI particles can be stabilized by polymers, however **the attachment of stabilized nZVI to collector surfaces is still high**. This is probably due to a shifted contact frontier between the coated nanoparticles and collector grains, where electrical double layer interaction is weaker [1]. nZVI mobility in granular aquifers remains limited [2].

Previous work with polymer-coated Ag nanoparticles and fullerenes demonstrated that when a **coating polymer** was allowed to attach to **the collector surfaces**, **the attachment efficiency** of these nanoparticles and the collector **was reduced** due to electrosteric stabilization [2, 3].

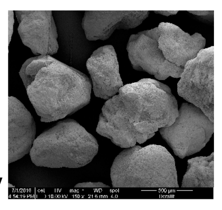
The aim of this study was to assess how the coating of collector surfaces with a polymer influences the attachment of nZVI used in groundwater remediation.

COLUMN EXPERIMENTS



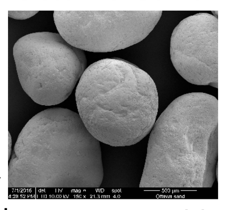
COLLECTORS

Dorsilit sand



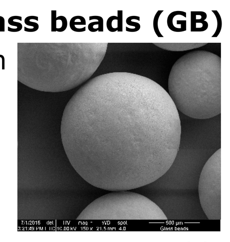
d_{50}: 0.65 mm
subangular
moderately well sorted
quartz
ζ‡: -24±2 mV
‡ measured in standard water
permeable rough

Ottawa sand†



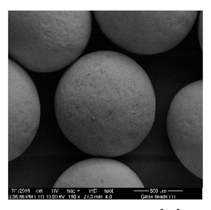
d_{50}: 0.67 mm
round
well sorted
quartz
ζ‡: -26±2 mV
† acid washed
permeable smooth

Glass beads (GB)



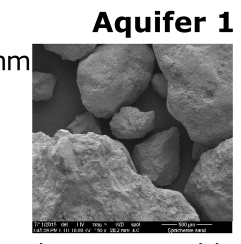
d_{50}: 1.00 mm
round
very well sorted
quartz
ζ‡: n. a.
permeable smooth

Ferrihydrite coated GB



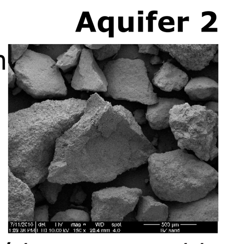
d_{50}: 1.00 mm
round
very well sorted
quartz
ferrihydrite
ζ‡: ca. -18 mV
permeable smooth

Aquifer 1



d_{50}: 0.80 mm
angular
poorly sorted
quartz
feldspar
Fe oxides
ζ‡: -14±2 mV
less permeable rough

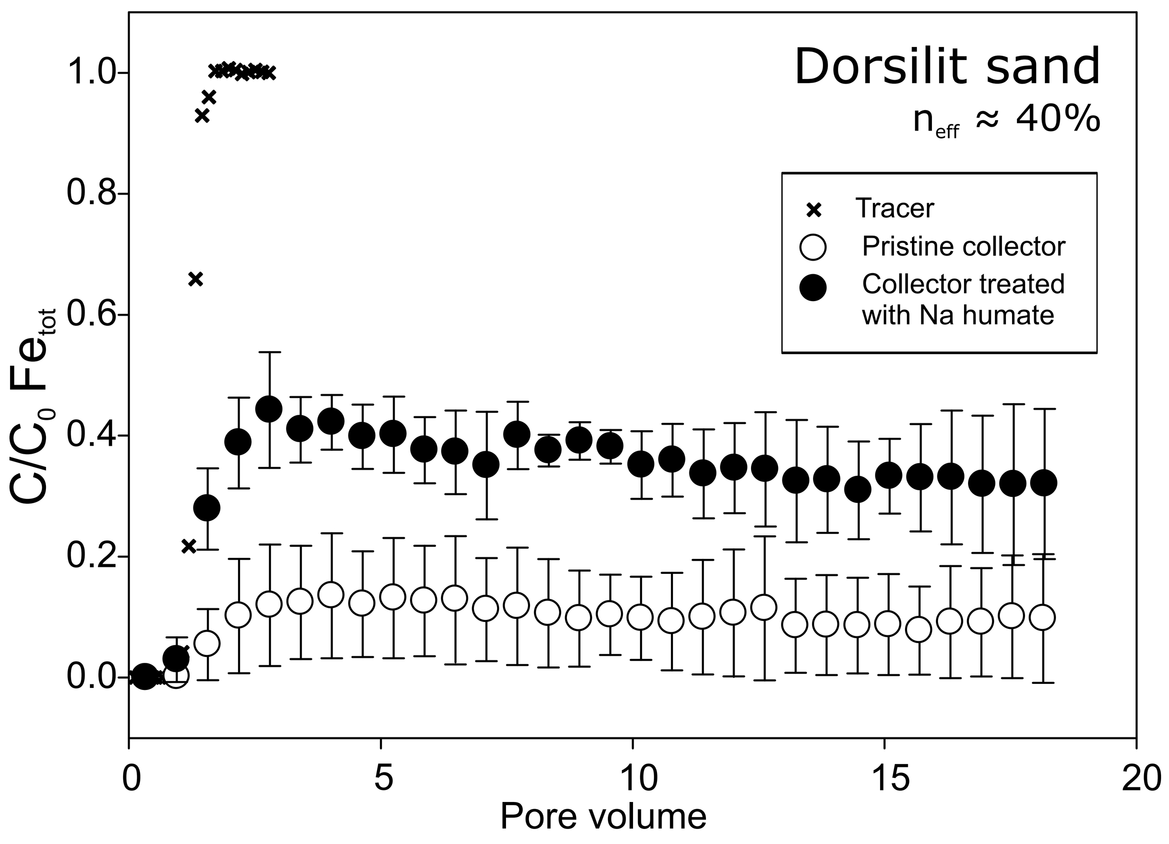
Aquifer 2



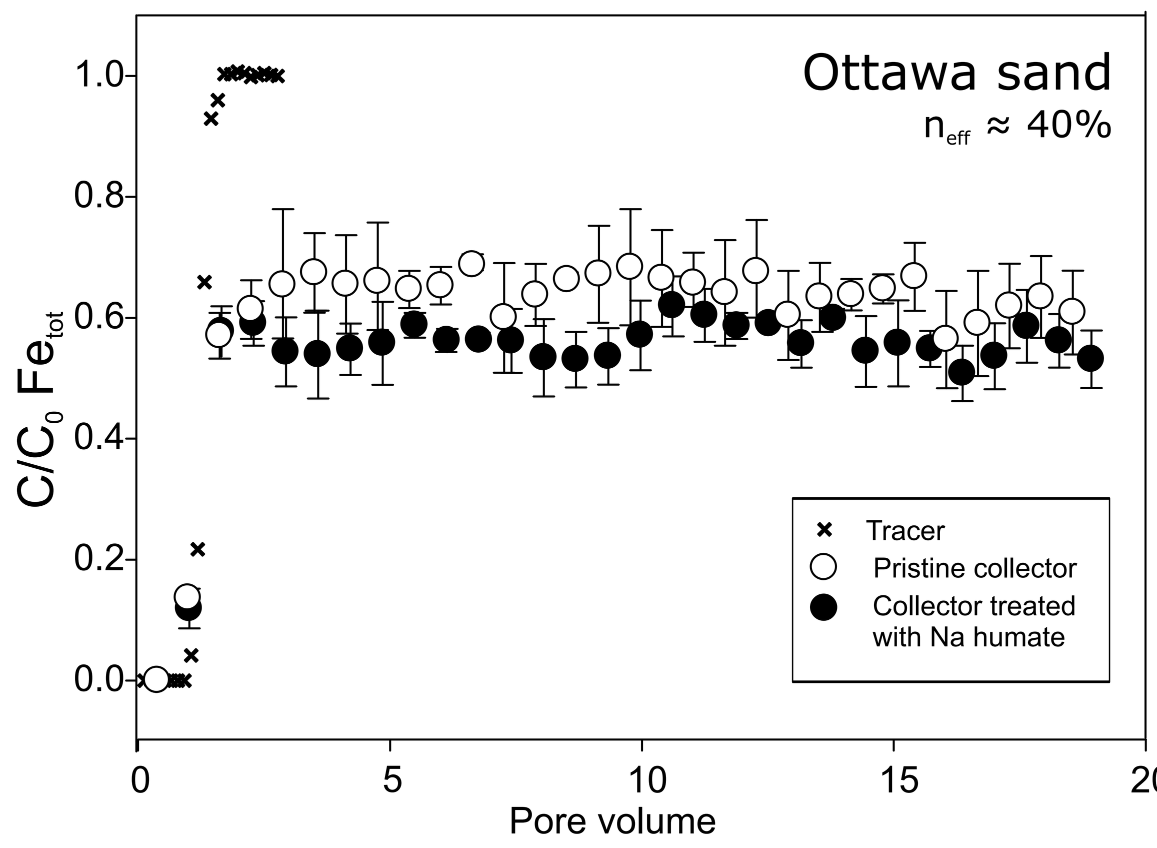
d_{50}: 0.48 mm
angular
poorly sorted
quartz
carbonate
ζ‡: -18±3 mV
less permeable rough

RESULTS

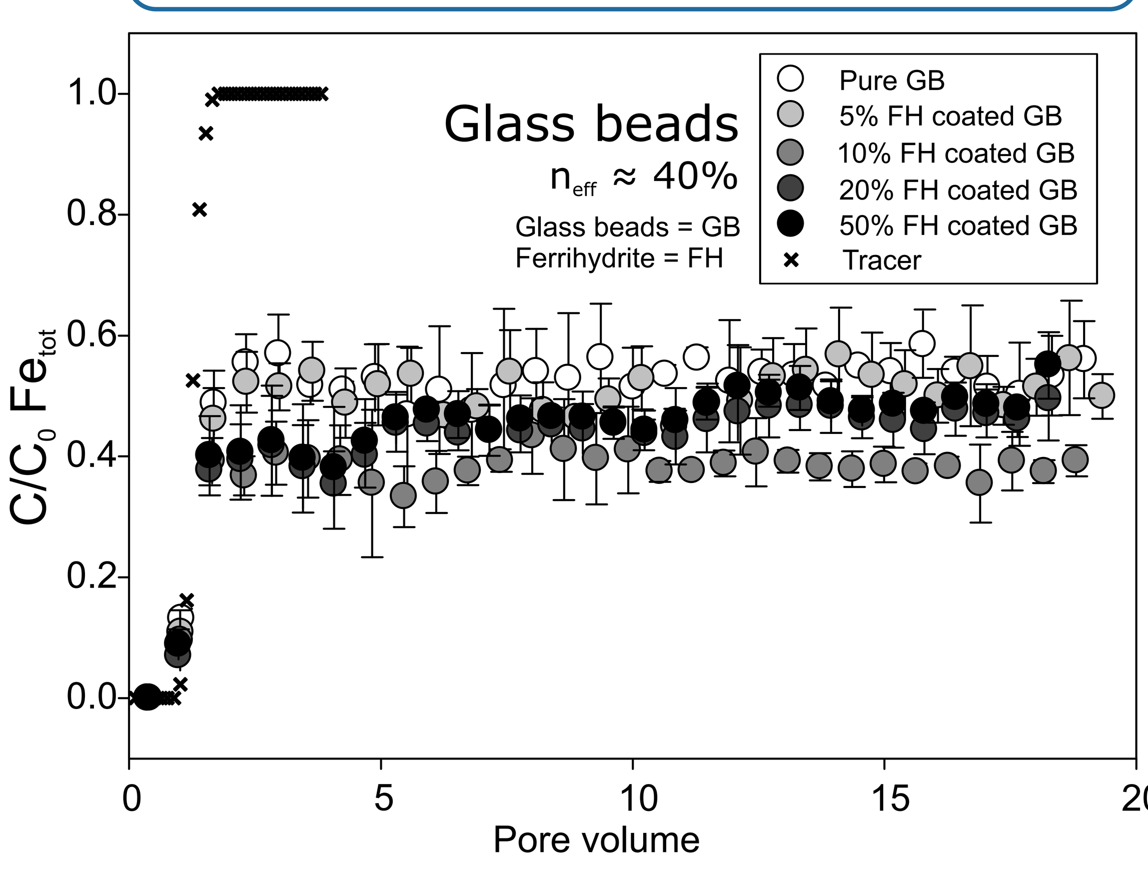
Na humate attaches to rough surfaces of permeable Dorsilit sand and increases (4-fold) nZVI breakthrough



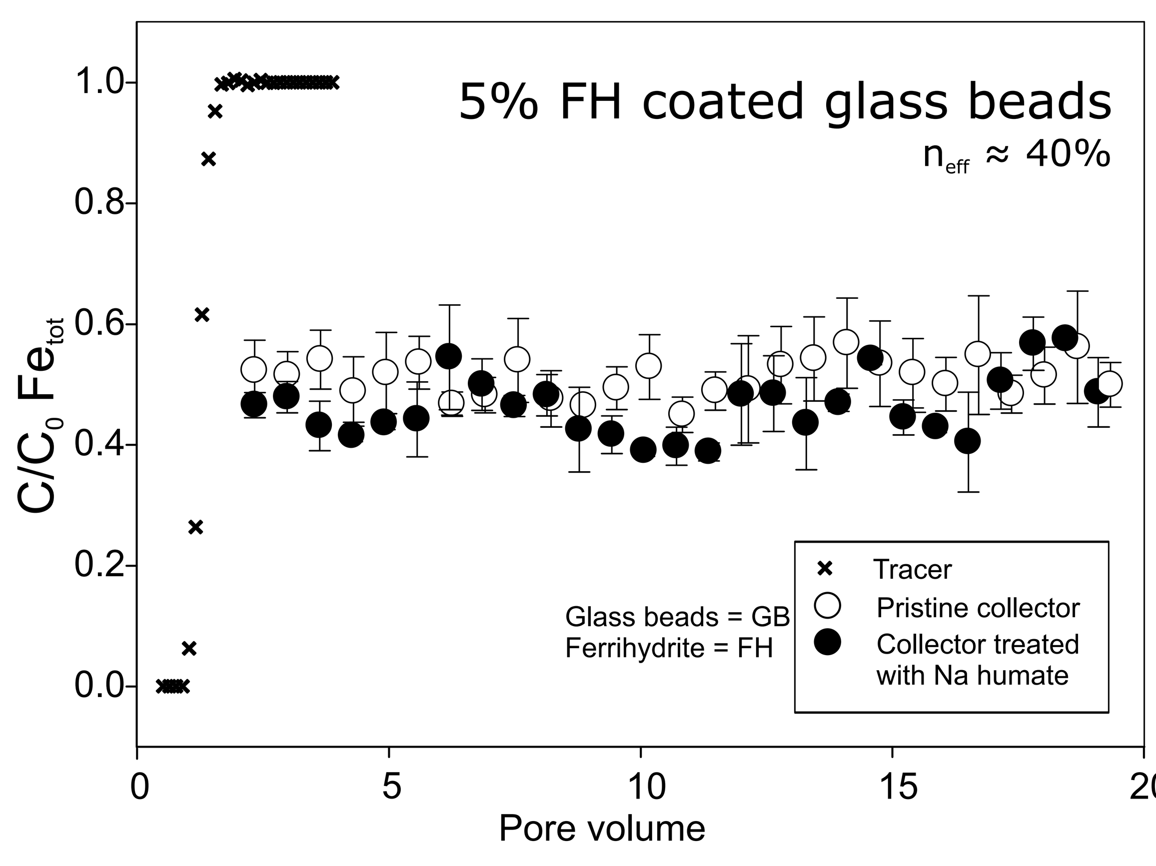
Na humate does not attach to smooth surfaces of Ottawa sand and does not affect nZVI breakthrough



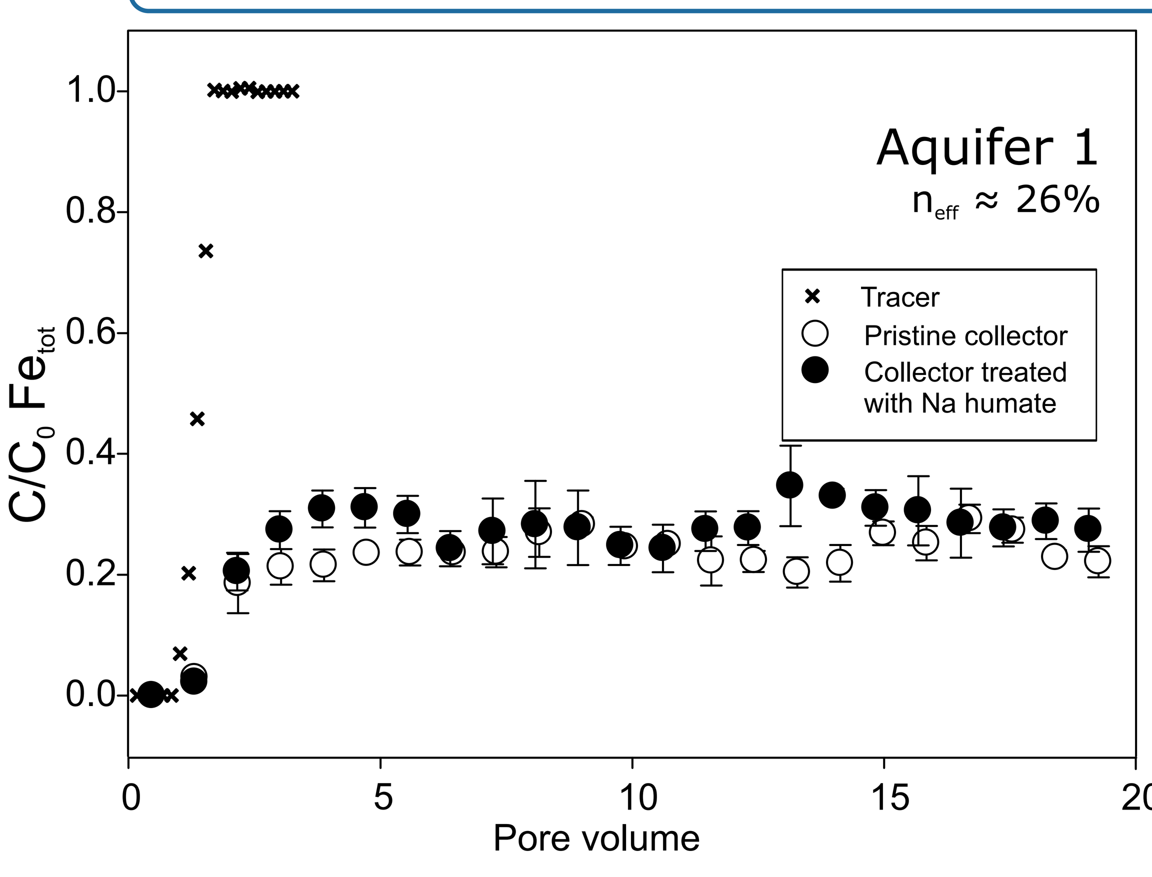
Bivalent cations in standard water undermine the effect of the surface charge heterogeneity which results in a similar nZVI breakthrough in all collectors

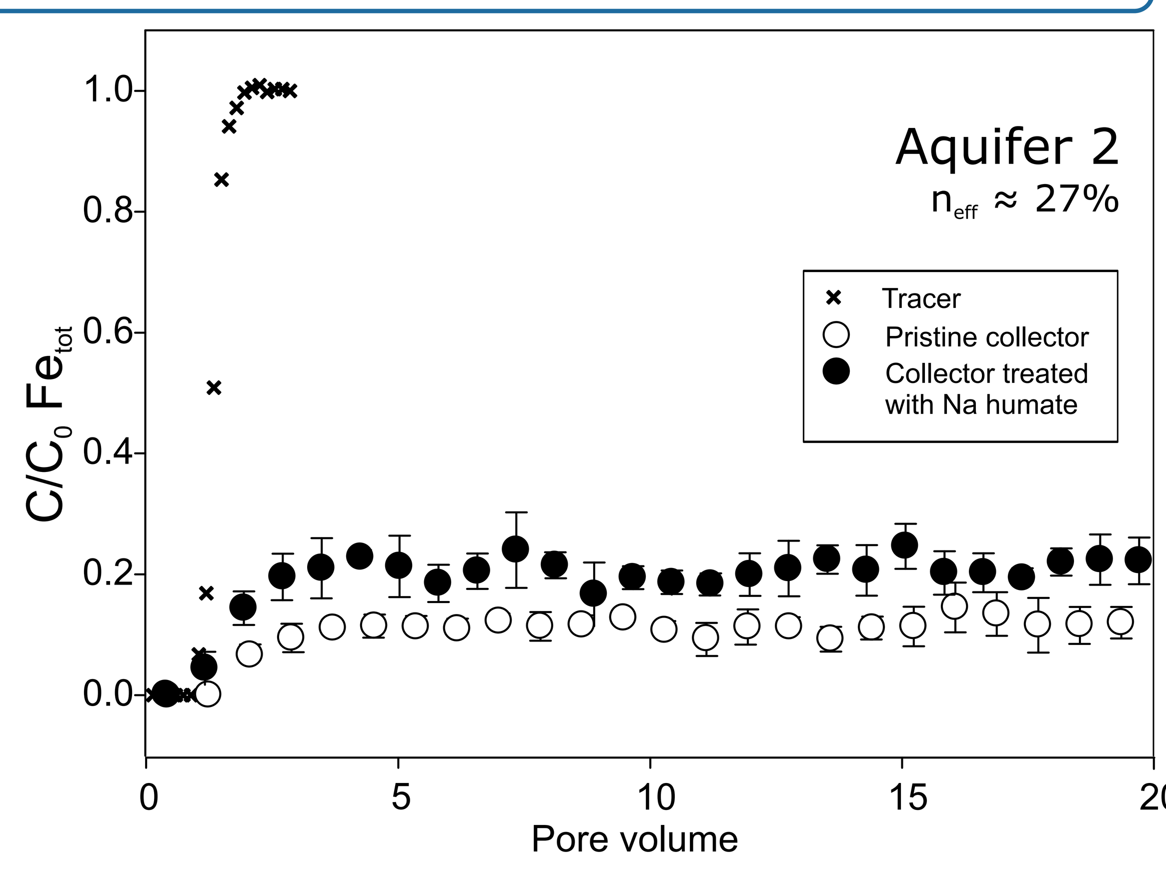


Na humate does not attach to smooth surfaces of glass beads with surface charge heterogeneity and does not affect nZVI breakthrough



Low permeability of collectors prevents an effective coating of collector surfaces with Na humate, which in turns does not affect the nZVI attachment





nZVI and Na humate

Standard water
With environmentally relevant ionic strength of 4.9 mM
$[Ca^{2+}]$:0.3 mM; $[Mg^{2+}]$:0.5 mM; pH: 7.7

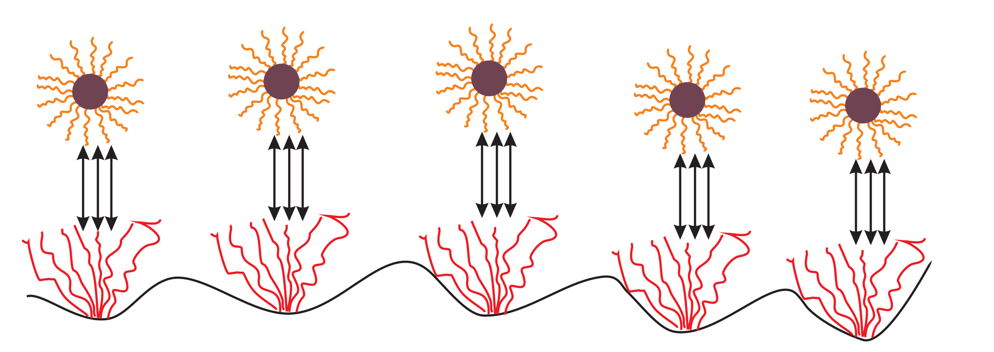
nZVI particles (NANOFER 25S, Nanoiron, s.r.o., CZ)
Coated with polyacrylic acid

nZVI suspension in standard water
nZVI concentration: 1 g/L; ζ: -24.2 ± 4.5 mV
nZVI size distribution [μm]: $d_{10}|d_{50}|d_{90}$=1.7│5.8│31.6

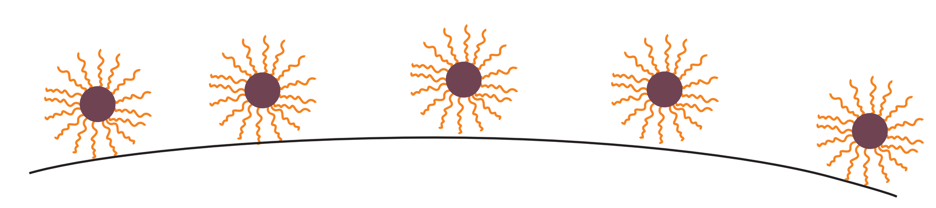
Na humate (HUMIN-S 775, Humintech® GmbH, GER)
Na salt of humic acid derived from an oxidation product of lignite, leonardite
Concentration in standard water: 10 mg/L

CONCLUSIONS

- A permeable silica collector with rough surfaces allows homogeneous attachment of Na humate, which provides electrosteric stabilization and hinders deposition of polymer coated nZVI onto collector grains.



- Na humate does not attach to smooth surfaces of the silica collector grains. Polymer coated nZVI attaches to collector grains as a consequence of a shifted contact frontier, where electrical double layer interaction is weaker, as has been observed for Ag nanoparticle [1].



- Na humate does not attach to smooth surfaces of the collector grains, even if the surface contains charge heterogeneity (such as ferrihydrite patches on glass beads).
- In low permeable natural collectors Na humate does not attach effectively, even to rough surfaces of the collector grains which contain surface charge heterogeneity (such as Fe oxide and carbonates), and is not able to prevent the attachment of nZVI.

References

[1] Lin, S.H., Cheng, Y.W., Liu, J. and Wiesner, M.R. (2012) Polymeric Coatings on Silver Nanoparticles Hinder Autoaggregation but Enhance Attachment to Uncoated Surfaces. Langmuir 28(9), 4178-4186.

[2] Laumann, S., Micić, V., Lowry, G.V. and Hofmann, T. (2013) Carbonate Minerals in Porous Media Decrease Mobility of Polyacrylic Acid Modified Zero-Valent Iron Nanoparticles used for Groundwater Remediation. Environmental Pollution 179, 53-60.

[3] Chen, K.L. and Elimelech, M. (2008) Interaction of Fullerene (C-60) Nanoparticles with Humic Acid and Alginate Coated Silica Surfaces: Measurements, Mechanisms, and Environmental Implications. Environmental Science & Technology 42(20), 7607-7614.

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http://www.nanorem.eu