

Colloidal Fe-zeolites - A novel material for sorption-supported in-situ chemical oxidation (ISCO)

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Introduction:

Fe-containing zeolites are a promising material for the removal of organic contaminants from groundwater, since they can be tailored for an optimal combination of two functions: I) Zeolites with appropriate channel structure and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio have excellent adsorption efficiencies for small organic molecules such as MTBE, BTEX or chlorinated solvents. II) The ion exchange sites located in the pore channels and cages of zeolites allow dispersion and stabilization of isolated iron ions, which are highly active in redox reactions. Thus, Fe-loaded zeolites have been shown to function as heterogeneous Fenton-like catalysts over a wide pH range including neutral conditions [1-3].

With respect to *ex-situ* treatment of contaminated groundwater, Fe-zeolites can be an interesting alternative to activated carbon since Fe-zeolite adsorbers offer the option of easy on-site regeneration by flushing with H_2O_2 solution [1]. In the framework of the EU project NanoRem a novel concept for *in-situ* chemical oxidation based on the application of colloidal Fe-zeolites is developed (Figure 1). The basic idea is to apply a solid adsorbent and catalyst for Fenton-like oxidation in the form of a suspension, which can be injected into the aquifer in an initial step, separate from the subsequent addition of H_2O_2 . The colloidal particles are transported over a certain distance and deposited on the aquifer sediment, where they form an active zone in the preferred groundwater flow paths. Using a stationary solid catalyst has the advantage to allow a mixing with the oxidant in the subsurface, i.e. at the location of the contamination.

By this means, the injection of mixtures of catalyst and H_2O_2 , causing vigorous reactions and thus safety issues known from conventional Fenton-based ISCO, could be avoided. In addition, prior to oxidant injection the Fe-zeolite zone could be initially used as a sorption barrier. By this means aqueous phase concentrations of contaminants are reduced and further spreading of plumes is prevented. At the same time, the sorption barrier can enrich contaminants from a larger volume of water before injecting the oxidant into it. This would correspond to an increased radius of influence of the ISCO process and a more efficient utilization of H_2O_2 .

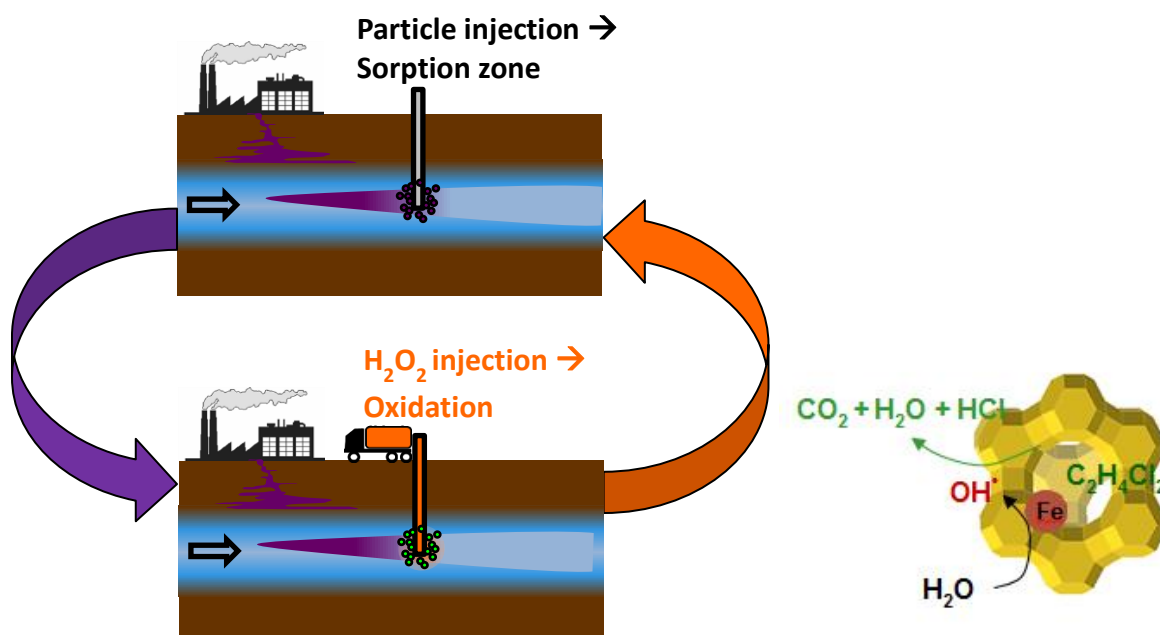


Figure 1: Schematic presentation of application of colloidal Fe-zeolites for construction of in-situ sorption and reaction zones

Results:

This contribution summarizes results from lab experiments on the selection and optimization of Fe-zeolites with respect to transport and distribution in saturated porous media as well as adsorption and catalytic oxidation of various groundwater contaminants (MTBE, trichloroethene (TCE), 1,2-dichloroethane (DCA) and toluene). Structure-property correlations were derived by screening various zeolite types differing in framework type and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for adsorption of model contaminants. Channel diameter (determined by the framework type) and surface hydrophobicity (determined by $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) are the most influential factors in this process. Even though high-silica zeolites have a low ion-exchange capacity and thus can take up only limited amounts of iron ions, it was possible to obtain sufficiently active catalysts for oxidation of adsorbed contaminants by H_2O_2 [3].

Soluble (modified) biopolymers were applied in order to obtain appropriate suspension stability of the colloidal zeolites (Figure 2). Due to the fact that these soluble polymers are excluded from the inner pore volume of the zeolites by virtue of their size, no significant adverse effects on contaminant adsorption and catalytic performance of the Fe-zeolites are observed.

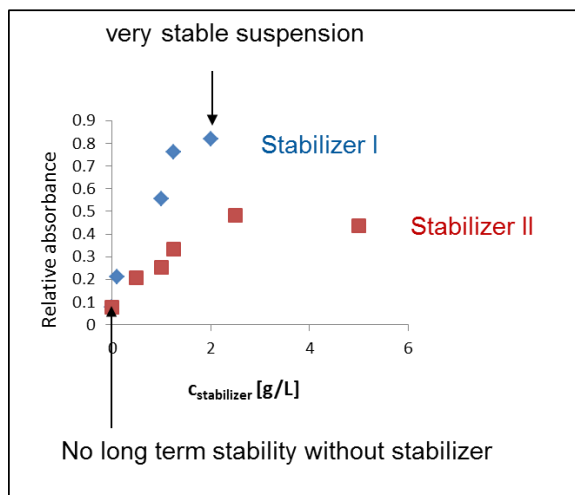


Figure 2: Left: Percentage of particles remaining in suspension after 24 h ($c_{\text{Zeolite}} = 2.5 \text{ g L}^{-1}$, 10 mM KNO_3) determined by turbidity measurement at a height of 19 mm below water table; Right: Powder and suspension of Fe-BEA-35

Particle mobility was studied in 1D-column experiments using standard materials (porous media and water) and protocols developed in the NanoRem project. For stabilized Fe-BEA-35 (the first prototype Fe-zeolite selected), promising results on mobility were obtained (Figure 3), showing breakthrough of 85% particle mass concentration from a 20 cm column (washed quartz sand 0.3 - 0.8 mm, soft water, $u = 10 \text{ m d}^{-1}$, $c_{\text{particle, in}} = 1 \text{ g L}^{-1}$, $c_{\text{stabilizer}} = 1.5 \text{ g L}^{-1}$).

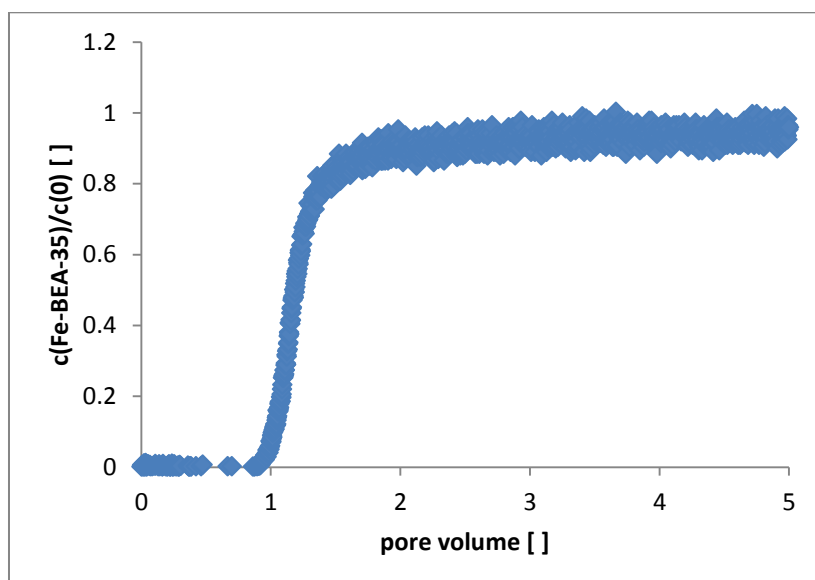


Figure 3: Breakthrough curve of Fe-BEA-35 in a column experiment: column ($l = 20 \text{ cm}$, $d = 1 \text{ cm}$, filled with washed quartz sand (Dorsilit 8, $d_{10} - d_{90} = 0.36 - 0.88 \text{ mm}$), $c_{\text{Fe-BEA-35}} = 1 \text{ g L}^{-1}$, $c_{\text{stabilizer}} = 1.5 \text{ g L}^{-1}$, soft water (U.S. EPA [4]), $u = 10 \text{ m d}^{-1}$).

In batch experiments Fe-BEA-35 showed high degrees of adsorption for all tested model contaminants whereby sorption coefficients K_d correlate with the octanol-water partition coefficients K_{ow} of the compounds (Table 1 and Figure 4). Fe-BEA-35 showed high catalytic activity in Fenton-like oxidation even in very hard water (pH 8.2). Reaction rates of the model contaminants were increasing in the order DCA < MTBE < TCE < toluene, which is in accordance with the selectivity predicted for a reaction driven by OH-radicals (Table 1 and Figure 4).

Table 1: Adsorption of model contaminants on Fe-BEA-35 in stabilized suspension (sorbed fraction X_{sorb} and sorption coefficient K_d at $c_{Fe-BEA-35} = 50 \text{ g L}^{-1}$ and $c_{total, substrate} = 25 \text{ mg L}^{-1}$, $c_{stabilizer} = 5 \text{ g L}^{-1}$) and kinetics of contaminant degradation by subsequent addition of $8 \text{ g L}^{-1} \text{ H}_2\text{O}_2$ (pseudo-first-order rate constant for initial reaction period k' and oxidant utilization efficiency $R_{ox,90} = \text{mol oxidant consumed per mol contaminant degraded until 90\% contaminant degradation was reached}$). Literature data for octanol-water partition coefficient ($\log K_{ow}$) and rate constants for reaction with OH-radicals for (k_{OH}) comparison.

Substrate	$\log K_{ow}^{[5]}$	$X_{sorb} [\%]$	K_d	$k' [\text{min}^{-1}]$	$k_{OH} [\text{M}^{-1} \text{s}^{-1}]^{[6]}$	R_{ox}
DCA	1.47	96.2	506	0.023	0.2 - 0.7	47
MTBE	1.24	98.5	1313	0.038	1.6	33
TCE	2.42	99.3	2837	0.051	2.9 - 4.3	38
toluene	2.69	99.7	6647	0.090	3.0 - 5.1	16

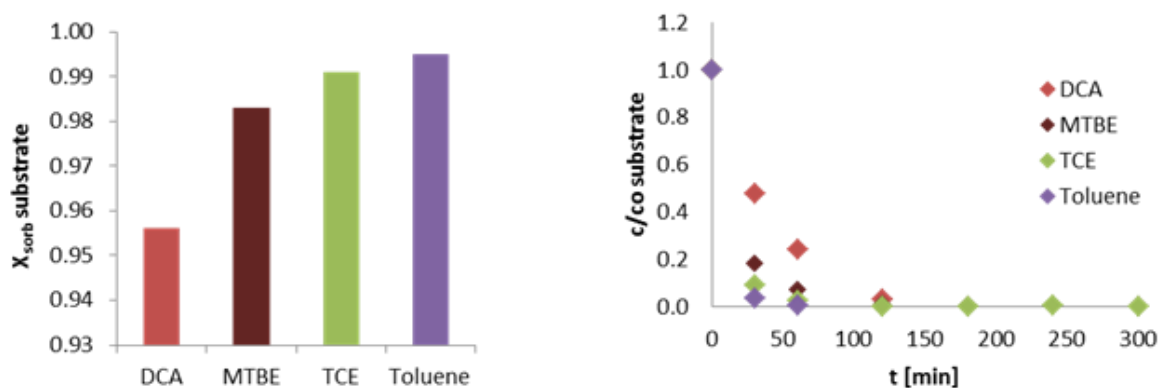


Figure 4: Sorbed fraction (Left) and kinetics of degradation (Right) of various model contaminants at $c_{Fe-BEA-35} = 50 \text{ g L}^{-1}$, $c_{substrate} = 25 \text{ mg L}^{-1}$ each, $c_{stabilizer} = 5 \text{ g L}^{-1}$, start of reaction: $c_{H_2O_2} = 8 \text{ g L}^{-1} \text{ H}_2\text{O}_2$, pH = 7

In addition, column experiments simulating the cycle of catalyst infiltration and immobilization, contaminant adsorption and degradation were conducted using MTBE as model contaminant. Fe-BEA-35 which was loaded on washed quartz sand at a mass fraction of 1 wt% showed stable adsorption and catalytic properties over three cycles of infiltration of MTBE-contaminated water (10 mg

L⁻¹ MTBE in very hard water, $u = 1 \text{ m d}^{-1}$) with intermittent regeneration by H₂O₂ infiltration (10 g L⁻¹ H₂O₂ in very hard water, $u = 1 \text{ m d}^{-1}$).

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References:

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