Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Fe-Zeolites as Catalysts for Wet Peroxide Oxidation of Organic Groundwater Contaminants: Mechanistic Studies and Applicability Tests

Anett Georgi[a]; Rafael Gonzalez-Olmos[a]; Robert Köhler[a]; Frank-Dieter Kopinke[a]
[a] Helmholtz Centre for Environmental Research - UFZ, Department of Environmental Engineering, Permoserstrasse, Leipzig, Germany

To cite this Article Georgi, Anett , Gonzalez-Olmos, Rafael , Köhler, Robert and Kopinke, Frank-Dieter(2010) 'Fe-Zeolites as Catalysts for Wet Peroxide Oxidation of Organic Groundwater Contaminants: Mechanistic Studies and Applicability Tests', Separation Science and Technology, 45: 11, 1579 — 1586

To link to this Article: DOI: 10.1080/01496395.2010.487466

URL: http://dx.doi.org/10.1080/01496395.2010.487466

Separation Science and Technology, 45: 1579–1586, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.487466

Fe-Zeolites as Catalysts for Wet Peroxide Oxidation of Organic Groundwater Contaminants: Mechanistic Studies and Applicability Tests

Anett Georgi, Rafael Gonzalez-Olmos, Robert Köhler, and Frank-Dieter Kopinke
Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Engineering, Permoserstrasse, Leipzig, Germany

Two types of iron-containing zeolites, Fe-ZSM5 and Fe-Beta, were tested as catalysts for wet peroxide oxidation of organic groundwater contaminants such as trichloroethene (TCE) and methyl tert-butyl ether (MTBE) at nearly neutral pH. Adsorption of TCE is more favorable on the ZSM5 zeolite whereas MTBE is effectively adsorbed on Beta zeolite. Batch experiments showed that the efficiency of utilization of H_2O_2 for contaminant degradation is more favorable for the catalyst with the higher adsorptive enrichment of the respective contaminant. Laboratory-scale column experiments, including the use of contaminated groundwater, were conducted in order to test the stability of the Fe-zeolites under flow-through conditions.

Keywords adsorption; Fenton-like; hydrogen peroxide; iron-containing zeolites; wet peroxide oxidation

INTRODUCTION

In recent years, increasing attention has been paid to heterogeneous Fenton-like systems, including solid iron oxides as well as iron species immobilized on solid supports such as zeolites, mesoporous solids, or Nafion membranes (1–8). Zeolites possess unique sorption properties with respect to smaller organic molecules; these properties make them interesting candidates as adsorbents and catalyst carriers in water treatment processes. In contrast to activated carbon, zeolites are not subject to oxidative degradation, even if hydroxyl radicals are involved. Adsorption affinity and capacity with respect to a certain compound depend on the hydrophobicity of the adsorbate and zeolite as well as the congruence of molecule and pore sizes. These sorption properties can be utilized in the case of Fe-zeolite catalysts for favored enrichment of the target organic contaminants in the vicinity of the catalytic centers.

For the technical realization of an oxidation process using Fe-zeolites as catalyst, adsorption and reaction can be combined in

I. a continuous or
II. an intermittent operation mode.

In mode (I), H_2O_2 is continuously fed to the contaminated water stream which enters the reactor. In mode (II), the contaminants are removed from the water primarily by means of adsorption on the Fe-zeolite combined with intermittent regeneration of the spent adsorbent by flushing with H_2O_2 solution. While several authors have reported promising results on the use of Fe-zeolites for contaminant degradation in batch experiments, e.g. (2,3,6), there is only very limited information about the long-term stability of these catalysts in flow-through systems (7). Recently, Fe_2O_3/SiO_2 catalysts have been studied for wet peroxide oxidation in fixed-bed flow-through reactors (9–11). Long-term activity has been demonstrated for Fe_2O_3 supported over mesostructured SBA-15. However, the stability of the catalytic activity obviously depends on the type of wastewater to be treated (9,10). The partial deactivation of the catalyst during long-term application for treatment of a phenolic wastewater was ascribed to a chemical alteration of the crystalline iron oxides supported over SBA-15 rather than to poisoning by carbonaceous deposits or iron complexation with acidic organic oxidation by-products (9).

This work is focused on Fe-zeolites as catalysts for wet peroxide oxidation. It combines mechanistic studies on the role of adsorption in contaminant degradation with column studies on the practical applicability of the Fe-zeolites for the treatment of contaminated water, including groundwater. Laboratory-scale column experiments in the continuous and intermittent operation modes were conducted for the degradation of trichloroethene (TCE) and methyl tert-butylether (MTBE), two frequently occurring groundwater contaminants.

Received 5 December 2009; accepted 12 February 2010.

Address correspondence to Anett Georgi, Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Engineering, Permoserstrasse 15, 04318 Leipzig, Germany. Tel.: +49 341 2351760; Fax: +49 341 2351471. E-mail: anett.georgi@ufz.de

EXPERIMENTAL

Materials and Methods

The applied Fe-zeolites were provided by Süd-Chemie Zeolites (Bitterfeld, Germany). They were produced by post-synthesis iron ion-exchange. Two Fe-zeolites in powder form were used: Fe-ZSM5 (Fe-content: 2.2 wt%, SiO_2/Al_2O_3 molar ratio: 26, particle size: $d_{50} = 6.4\,\mu m$, $d_{90} = 12\,\mu m$) and Fe-Beta (Fe-content after a pre-washing step (6): 0.97 wt%, SiO_2/Al_2O_3 molar ratio: 42, particle size: $d_{50} = 1.0\,\mu m$, $d_{90} = 2.1\,\mu m$). Furthermore, a pelletized material was used as received: Fe-Beta pellet (Fe-content: 3.1 wt%). X-ray fluorescence (XRF) measurements of the zeolites were done using a WDXRF-spectrometer S4 PIONEER (Bruker-AXS) as described elsewhere (6).

H_2O_2 content was determined by photometric measurements using titanyl sulphate. For determination of Fe(II/III) in aqueous samples a photometric test (Spectroquant, Merck) was used. The concentration of chloride and chlorinated acetic acids was determined by ion chromatography (IC) with conductivity detection using an AS19 column (Dionex). The concentrations of MTBE and TCE in water were determined by GC-MS analysis. For the analysis of MTBE and TCE in the column effluents, a headspace method using gas-tight syringes (100 µl) was applied. In the batch experiments aliquots of the reaction suspension were extracted using dichloromethane and the extracts were analyzed. For determination of the total organic carbon (TOC) content in aqueous samples, a carbon detector consisting of a combustion step and NDIR detection unit was applied (6). In order to remove inorganic carbon prior to analysis, samples were acidified ($pH \leq 5$) and purged with N_2 for 5 min. Due to the fact that the purging can result in a loss of volatile organic compounds, the obtained TOC value has to be considered as a lower limit.

Batch Experiments for Determination of Adsorption Isotherms and Testing of the Degradation of the Model Contaminants

The equilibrium sorption isotherms were measured at ambient temperature (25 ± 2°C). They were obtained by preparing several suspension samples with different concentrations of zeolite and different total concentrations of the analyte (either MTBE or TCE) in 250 mL-flasks with Mininert® valves. The samples were shaken on a horizontal shaker for 24 hours. This procedure proved to be sufficient to reach the adsorption equilibrium (6). Afterwards, the concentration of the freely-dissolved fraction of the analyte was determined by headspace analysis.

The batch degradation experiments were conducted at ambient temperature (25 ± 2°C). An aqueous solution containing one of the model contaminants (MTBE or TCE) was filled into a 120 mL-flask with a Mininert® valve for headspace sampling and an additional valve which could be used to depressurize the reactor and to add reagent solutions. After adding the catalyst to the reactor, the pH of the suspension was adjusted to 7 and readjusted during the reaction if necessary by adding dilute NaOH. Adsorption was allowed to come to equilibrium for at least 24 h, while the samples were shaken on a horizontal shaker. Afterwards, the concentration of the freely dissolved fraction of the organic compounds was determined by headspace analysis. The reaction was started by adding a defined amount of H_2O_2 solution (30 wt%). The concentration of H_2O_2 was monitored by photometry as explained above. In order to keep the concentration of H_2O_2 approximately constant (±20% of the starting value), further H_2O_2 was periodically added into the reactor. The total residual concentration of the model contaminants during the reaction was determined by solvent extraction of aliquots of the reaction suspension and GC-MS analysis as described above.

Column Experiment for TCE Degradation on Fe-ZSM5 (Continuous Operation Mode)

A glass column (l = 20 cm, d = 1 cm) was filled with 11 g of Fe-ZSM5 (grain size: 0.5–1 mm) which had been pelletized by pressing (using a disk press) and gentle crushing of the sample disk followed by sieving of the material. The column was operated with deionized water or tap water spiked with TCE (25 or 100 mg/L) and H_2O_2 (100–600 mg/L) and adjusted to pH = 7. This solution was filled into a 5 L flask which was wrapped in black plastic foil. No degradation of TCE was observed in this reservoir. The reservoir was refilled before the volume of water was decreased by 20% in order to avoid excessive loss of TCE into the growing headspace volume. The water was pumped through the column in an upward direction using a piston pump. The column experiment was conducted at ambient temperature (25 ± 2°C). Aliquots of the column effluent were analyzed for the concentration of organic compounds and their degradation products as well as H_2O_2, leached iron and pH.

Column Experiment for MTBE Degradation on Fe-Beta (Intermittent Operation Mode)

The Fe-Beta pellet catalyst was crushed and sieved in order to obtain a size fraction of 0.25–0.63 mm. 5 g of this material was filled into a glass column (l = 10 cm, d = 1.2 cm). The column was operated with tap water (pH = 7.8) spiked with 4 mg/L MTBE or with groundwater from a contaminated site in Leuna (Saxony-Anhalt, Germany) which contains as main contaminants MTBE (about 4 mg/L) and benzene (about 20 mg/L) and has a pH of 7.5–7.8. The column experiment was conducted at ambient temperature (25 ± 2°C). Before feeding into the Fe-zeolite column, the groundwater was slightly aerated in order to facilitate complete degradation of benzene by the autochthonous bacteria (residual concentration $<0.05\,mg/L$). The concentration of MTBE was not affected by this step. Furthermore, a sand column ($l = 22\,cm$, $d = 2.4\,cm$, filled with quartz sand, 63–630 µm) was installed in front of the Fe-zeolite column in order to remove particles (e.g., precipitates) from the groundwater. The water was pumped through the column in an upward direction using a piston pump with a flow rate of 3.5 or 1.1 mL/min. Several adsorption/regeneration steps were run whereby the conditions were varied. In the regeneration steps the Fe-zeolite column was flushed in-circuit with a flow rate of 2 mL/min over 24 h using a 250 mL reservoir. The regeneration medium consisted of deionized water with 5 or 15 g/L of H_2O_2 which was adjusted to pH 3 (using HNO_3) or pH 8.5 (using NaOH). The pH 8.5 was chosen in order to facilitate the determination of inorganic carbon produced from MTBE oxidation, i.e., to trap it in the regeneration solution as bicarbonate. In detail the conditions were: 5 g/L H_2O_2, pH 8.5 in the regeneration prior to the succeeding adsorption steps 2–5; 15 g/L H_2O_2, pH 8.5 before step 6; and 15 g/L, pH 3 before steps 7–9. Before and after each regeneration step, the column was flushed with about 10 pore volumes of deionized water.

RESULTS AND DISCUSSION

Batch Experiments

The adsorption studies clearly show the importance of the congruence of molecule size and pore diameter of the zeolites. Adsorption of TCE (kinetic diameter $d_{kin} = 5.6\,\text{Å}$, (12)) is more favorable at the ZSM5 zeolite also having a maximum pore diameter of 5.6 Å (13). In contrast, the bulkier MTBE molecule ($d_{kin} = 6.2\,\text{Å}$, (12)) is effectively adsorbed on the Beta zeolite having a larger maximum pore diameter of 7.5 Å (13). Figure 1 shows the adsorption isotherms of TCE and MTBE on Fe-Beta and Fe-ZSM5 with their Freundlich isotherm fits according to Eq. (1), where K_F $[(mg/kg)/(mg/L)^{1/n}]$ and $1/n$ are Freundlich parameters and q and c_{free} are the equilibrium concentration of the adsorbate in the solid phase (mg/kg) and liquid phase (mg/L), respectively.

$$q = K_F\, c_{free}^{1/n} \tag{1}$$

The values of the Freundlich coefficients $1/n > 1$, as found for three out of four sorption isotherms, indicate a positive effect of adsorbate loading on the adsorption affinity. This behavior is classified as adsorption isotherm of type III or V (14). In mechanistic terms these isotherm types indicate that once a molecule has become adsorbed at a primary adsorption site, the adsorbate-adsorbate interactions significantly increase the driving force of the further adsorption process. Nevertheless, within the concentration range studied, the isotherms of MTBE and TCE adsorption on Fe-ZSM5 and Fe-Beta can be reasonably well described by the Freundlich model.

Both catalysts are able to produce reactive species from H_2O_2 at nearly neutral pH, facilitating the degradation of organic contaminants. This is especially important for the treatment of contaminated groundwater, which has a high buffer capacity and thus could only be acidified by means of large amounts of acid. The decomposition of H_2O_2 on Fe-ZSM5 and Fe-Beta follows a pseudo-first-order kinetics (6): $\ln(c/c_0) = -k \cdot t$, with c/c_0 as the relative residual concentration of H_2O_2 after a certain time (t) and k as the pseudo-first-order rate constant. The catalyst activity for H_2O_2 decomposition ($A_{H_2O_2}$), calculated as the ratio of the pseudo-first-order rate constant of H_2O_2 decomposition and the applied catalyst concentration ($A = k/c_{catalyst}$), is $3.7 \cdot 10^{-3}\,L/(g\,min)$ for Fe-ZSM5 whereas for Fe-Beta it is lower by about two orders of magnitude ($3.0 \cdot 10^{-5}\,L/(g\ min)$) (6). The respective catalyst activities related to the concentration of zeolite-supported iron are $0.17\,L/(g_{Fe}\,min)$ for Fe-ZSM5 and $0.0031\,L/(g_{Fe}\,min)$ for Fe-Beta.

In batch experiments, the degradation rate and the efficiency of H_2O_2 utilization for the degradation of the

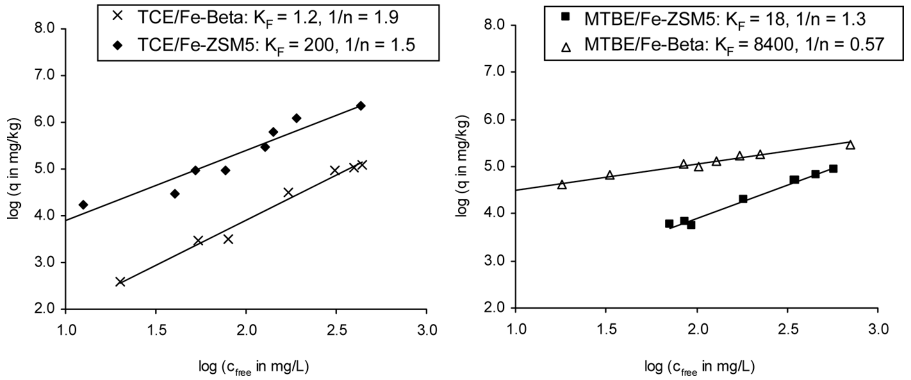


FIG. 1. Adsorption isotherms of TCE (left side) and MTBE (right side) on Fe-Beta and Fe-ZSM5, lines represent Freundlich isotherm fits, with K_F $[(mg/kg)/(mg/L)^{1/n}]$ and $1/n$ as Freundlich parameters according to $q = K_F\, c_{free}^{1/n}$.

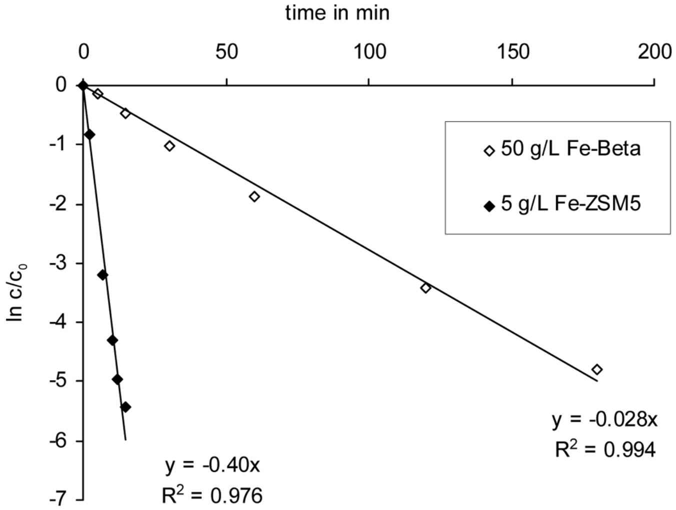


FIG. 2. Pseudo-first-order plot of the degradation of TCE ($c_0 = 50$ mg/L) in the presence of 7 g/L H_2O_2 and 50 g/L Fe-Beta or 5 g/L Fe-ZSM5, respectively.

two compounds MTBE and TCE at pH 7 with the different catalysts were studied. Under the applied conditions, the observed degradation kinetics can be reasonably well fitted by a pseudo-first-order kinetics, as it is shown in Fig. 2 for the degradation of TCE. It could be confirmed that leached metal species do not significantly contribute to the observed catalytic activity of the Fe-zeolites. No degradation of MTBE and TCE in the presence of H_2O_2 was observed if the catalyst was removed from the suspension by centrifugation. Table 1 shows the catalyst activities for the degradation of the two model compounds as calculated from the pseudo-first-order rate constants observed in batch experiments with Fe-ZSM5 and Fe-Beta, respectively. It is reasonable to assume that a lower activity in H_2O_2 decomposition leads to a proportionally lower steady-state concentration of hydroxyl radicals (or any other reactive species formed from H_2O_2). Therefore, it is plausible that the activity for contaminant degradation is generally lower for Fe-Beta than for Fe-ZSM5 (Table 1).

Besides the rate of contaminant degradation, the efficiency of H_2O_2 utilization for contaminant degradation is an important factor. Therefore, the moles of H_2O_2 consumed per mol of contaminant degraded were calculated for the initial reaction period, i.e., until the initial concentration of MTBE or TCE was reduced by 50%. The H_2O_2 consumption ratio was 59 and 36 for TCE with Fe-Beta and Fe-ZSM5, respectively, whereas for MTBE it was 78 and 310. From this comparison it becomes obvious that the utilization of H_2O_2 is more favorable in case of the catalyst with the better adsorption for the respective contaminant. This is plausible, since the enrichment of the contaminant in proximity to the catalytic sites will increase the probability of a reaction between the transient reactive species and the contaminant molecules.

The performance of a fixed-bed reactor containing Fe-zeolites for the degradation of a certain contaminant will be determined by the catalyst activity, the adsorption properties of the respective contaminant and the efficiency of H_2O_2 utilization for the desired degradation reaction. Based on the results of the batch adsorption and degradation experiments, Fe-ZSM5 was chosen as a catalyst for a first column test on TCE degradation, whereas Fe-Beta was selected for MTBE.

Column Experiment for TCE Degradation on Fe-ZSM5 (Continuous Operation Mode)

In the column test for TCE degradation in the continuous operation mode, a total volume of 43 L of artificially contaminated water was treated, corresponding to 2800 bed volumes. Iron concentrations in the range of 0.5 ± 0.3 mg/L were measured in the effluent during the entire column test. That means that about 10% of the initial iron content of the Fe-ZSM5 material (2.2 wt%) was leached, which is a tolerable degree of iron loss. However, the iron leaching did not level off during the column operation; this indicates that iron loss would continue during a prolonged operation. Thus, in a technical application a renewal of the iron impregnation of the zeolite can become necessary at certain intervals. The pH of the

TABLE 1

Results of batch experiments on the degradation of TCE and MTBE ($c_0 = 50$ mg/L) in catalyst suspensions (pH 7) containing 7 g/L H_2O_2: catalyst activity for contaminant degradation (A), sorbed fraction before start of the reaction (F_{ads}), moles of H_2O_2 consumed per mol of contaminant degraded until $(c/c_0)_{contaminant} = 0.5$ is reached. (The stoichiometric H_2O_2/contaminant ratio for complete mineralization is 6 and 30 for TCE and MTBE, respectively)

	Catalyst	$c_{catalyst}$ in g/L	A in L/(g_{Fe} min)	F_{ads}	mol H_2O_2/mol contam.
TCE	Fe-Beta	50	5.6×10^{-2}	0.40	59
	Fe-ZSM5	5	7.6	0.65	36
MTBE	Fe-Beta	50	1.7×10^{-2}	0.98	78
	Fe-ZSM5	5	1.9×10^{-1}	0.15	310

effluent was in the range of 2.9–3.5 depending on the buffer capacity of the water and the TCE concentration. For comparison, total dechlorination of 100 mg/L of TCE would produce 2.3 mM HCl which corresponds to pH 2.6 in deionized water. Under less acidic conditions the iron loss rate is expected to be lower. Although the heterogeneous catalysis should be clearly prevailing, the low pH and the presence of dissolved iron ions facilitate the contribution of a homogeneous Fenton to the observed TCE degradation.

During the column test the conditions were varied, gradually increasing the stress for the catalyst (phase 1–6, Table 2). The applied flow-rates of 0.5 to 1.5 mL/min correspond to mean residence times of the water in the column of 10 to 3.3 min, respectively. The TCE concentration was increased from 25 to 100 mg/L and H_2O_2 was added to the water in a molar ratio H_2O_2/TCE of 54 to 23, which equals the 7-fold to 3-fold stoichiometric amount for complete mineralization. Irrespective of the applied conditions, the TCE concentration in the column effluent was below the detection limit within a throughput of 40 L or 2600 bed volumes of contaminated water, representing a decontamination degree of >99.6%. Between an elution volume of 40 and 43 L (indicated as phase 6) the concentration in the effluent gradually increased up to a value of 0.5 mg/L (0.5% of inflow concentration). The yield of chloride in the effluent was about 85% in phase 1 and 2, but was slightly lower (about 70%) in phase 3–5 when the TCE inflow concentration was increased. The reduction in TOC was calculated from the ratio of the concentrations of organic carbon in the effluent and TCE carbon in the inflow. The TOC reduction was high (80–90%) in phase 3–5, but decreased in the last phase of column operation (61%).

The increase in the outflow concentrations of TCE and TOC in phase 6 points to a decline in catalyst activity. Possible reasons are the blockage of the catalyst surface by organic coatings resulting from incomplete oxidation of TCE or partial deactivation of the iron species by complexation with refractory oxidation by-products such as carboxylic acids. TOC analysis of the column material revealed a slight increase in organic carbon (0.5 wt%). Inorganic precipitates (such as carbonates or hydroxides) are not likely at the acidic pH of the column effluent. Intervals with an oxidative regeneration under more severe conditions, i.e., flushing with higher H_2O_2 concentration or regeneration by thermal treatment in air (500°C), might be an option in order to remove organic residues completely.

Chlorinated acetic acids are known problematic intermediates in TCE oxidation by Fenton-like processes (15). It was only within phase 1 that the concentration of the chlorinated acetic acids was below the detection limit of the IC method (1 mg/L); during all other phases the concentration of mono- and dichloroacetic acid were in the range of 2–20 mg/L and 0.2–2.4 mg/L, respectively. Although mono- and dichloroacetic acid are degradable by Fenton-like processes, the rate constants for their reactions with OH-radicals are rather low, i.e., two orders of magnitude lower than for TCE (16). Furthermore, due to their hydrophilicity they have a much lower tendency to be adsorbed by the zeolite. This column experiment was designed to have a high throughput of water within a manageable total run time, thus allowing the stability of the catalyst to be evaluated. In order to decrease the concentration of chlorinated acetic acids in the effluent further, a considerably longer residence time of the water in the column would be necessary. This would require amendment of H_2O_2 at additional ports along the flow-path, in order to provide a sufficiently high H_2O_2 concentration over

TABLE 2

Results of the column test for TCE degradation with H_2O_2 on Fe-ZSM5: TCE concentration in the column effluent ($c_{TCE,out}$), yield of chloride as percentage of maximum theoretical yield (y_{Cl^-}) and reduction of TOC (R_{TOC}). Conditions such as TCE concentration at the inflow ($c_{TCE,in}$), flow rate, molar ratio of H_2O_2/TCE and type of water used (deionized water – DI, tap water – TW) were varied within phase 1–6 with V_{total} as the total volume of water eluted from the start of the column test until the end of the respective phase

Phase	V_{total} in L	Flow rate in mL/min	$c_{TCE,in}$ in mg/L	Water type	Molar ratio H_2O_2/TCE	$c_{TCE,out}$ in mg/L	y_{Cl^-} in %	R_{TOC} in %
1	14.0	0.5	25	DI	54	<0.1	86 ± 15	n.d.[a]
2	22.6	0.5	25	DI	27	<0.1	83 ± 17	n.d.
3	27.3	0.5	100	DI	23	<0.4	69 ± 10	90 ± 4
4	30.5	1.5	100	DI	23	<0.4	66 ± 5	90 ± 7
5	40.8	1.5	100	TW	23	<0.4	71 ± 15	83 ± 9
6	43.4	1.5	100	TW	23	0.5[b]	90[b]	61[b]

[a] Not determined.

[b] Final values at the end of phase 6.

the entire column length. On the other hand, an intermittent operation mode might be a more promising approach in such a case where the contaminant is efficiently adsorbed by the Fe-zeolite but the degradation of the contaminant to the desired products is slow.

Column Experiment for MTBE Degradation on Fe-Beta (Intermittent Operation Mode)

In the column experiment with the Fe-Beta pellet material 9 adsorption steps (10,000 bed volumes of water in total) were run, whereby the zeolite was regenerated by closed-circuit flushing with H_2O_2 solution. During the 24 h regeneration periods, the H_2O_2 was almost completely consumed. The MTBE concentration in the regeneration solution reservoir was in the range of 0.9–2 mg/L at the beginning of each regeneration step and was reduced to values below 0.1 mg/L within 24 h. Determination of TOC and inorganic carbon in the regeneration solution revealed that only a minor fraction of MTBE was mineralized: most of the MTBE carbon was still present as TOC (about 60 mg/L in the regeneration solution). Tert-butyl formate (TBF), tert-butyl alcohol (TBA), acetone, methyl acetate, alcohols $< C4$, carboxylic acids and formaldehyde are known intermediates of MTBE degradation (17,18). The regeneration solution was monitored after 24 h recycling for TBA and TBF, in order to meet the concerns related to their potential toxicity. However, their concentrations were below the detection limits of the headspace GC-MS method ($TBA \leq 2$ mg/L, $TBF \leq 0.5$ mg/L), showing that they did not significantly contribute to the observed TOC value. Hence, one can deduce that short-chain organic acids make the largest contribution to the remaining TOC value.

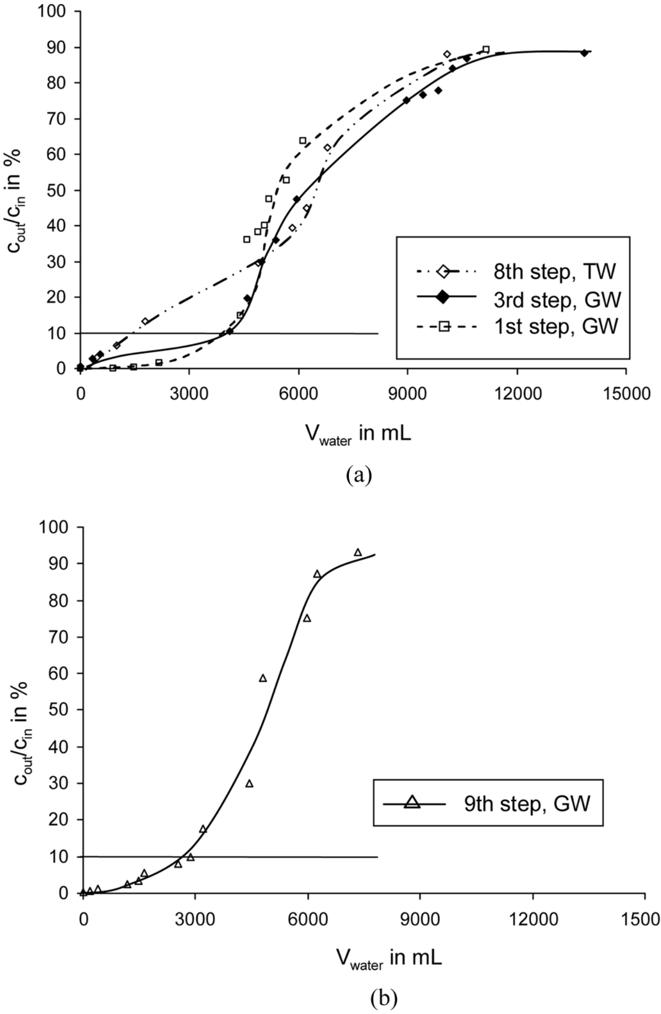


FIG. 3. Examples of breakthrough curves for MTBE obtained in a column experiment with artificially contaminated tap water (TW) and original contaminated groundwater (GW) within 9 adsorption steps, (a) steps 1, 3, 8 with water flow rate of 3.5 mL/min, (b) step 9 with flow rate of 1.1 mL/min. Column filling: 5 g Fe-Beta. Horizontal line represents hypothetical termination criterion of 10% MTBE breakthrough. c_{out} and c_{in} represent MTBE concentrations in the column outflow and inflow, respectively.

Within the 8 adsorption steps, the MTBE adsorption capacity of the zeolite remained nearly constant. The concentration of adsorbed MTBE at about 90% MTBE breakthrough varied only slightly and was between 4.8 and 5.6 mg/g. This proves that the catalyst was still sufficiently active to degrade the adsorbed MTBE completely in the regeneration steps over the whole operation period (10,000 bed volumes of water treated). Figure 3 shows exemplarily the breakthrough curves of MTBE in the adsorption steps 1, 3, 8, and 9. The figure illustrates that the breakthrough of MTBE starts earlier with an increasing number of adsorption/regeneration steps when otherwise identical conditions are applied. Considering a hypothetical termination criterion of 10% MTBE breakthrough, the fresh adsorber could be operated over a throughput of 410 bed volumes of water, but after repeated use the adsorber would have to be stopped and regenerated much earlier. The 10% breakthrough volume was affected by the regeneration conditions; however, even under the optimum conditions (regeneration solution with pH 3 containing 15 g/L H_2O_2) the 10% MTBE breakthrough occurred after only 150 bed volumes (8th adsorption step, Fig. 3). If the water flow rate is reduced by a factor of about 3, the breakthrough again becomes sharper for the used adsorber (9th adsorption step, Fig. 3), i.e., the 10% MTBE breakthrough is reached after 340 bed volumes. Obviously, the adsorption kinetics of MTBE on the zeolite is slowed down after repeated adsorption/regeneration. XRF analyses revealed an increase in the content of iron (from 3.2 to 4.2 wt%) and calcium (from 0.04 to 0.2 wt%) on the zeolite after the 9 adsorption-regeneration steps. The organic carbon content was only slightly increased (from 0.05 to 0.09 wt%).

Since the iron leaching of the Fe-Beta catalyst could not be determined in the column experiment with groundwater

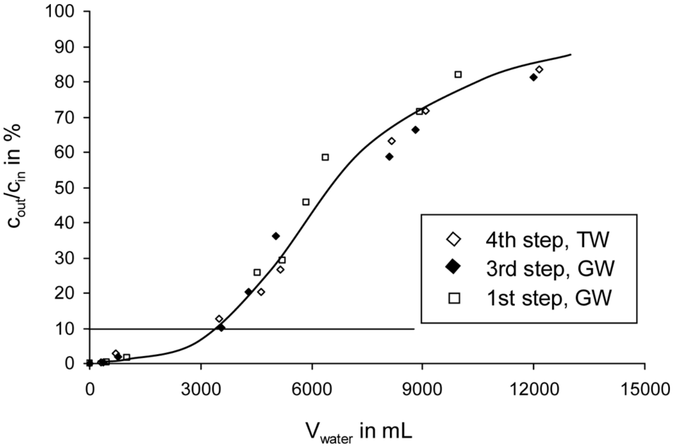


FIG. 4. Breakthrough curves for MTBE obtained in a column experiment with artificially contaminated tap water (TW) within 4 adsorption steps. Column filling: 5 g Fe-Beta. Water flow rate 3.5 mL/min. Horizontal line represents hypothetical termination criterion of 10% MTBE breakthrough. c_{out} and c_{in} represent MTBE concentrations in the column outflow and inflow, respectively.

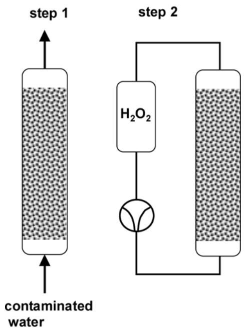
(increase in iron content due to precipitates) an additional column experiment using tap water (with low iron content) spiked with MTBE was conducted. Four consecutive breakthrough curves were recorded with intermittent recycling as described above for the experiment with groundwater. XRF analysis of the catalyst after this experiment revealed no significant change in the iron content, i.e., the iron leaching stability of the Fe-Beta catalyst is very good. Furthermore, the four MTBE breakthrough curves in the experiment with tap water showed identical shapes (Fig. 4). We did not observe any tendency towards pore blockage. Based on these results, we suggest that inorganic precipitates such as Fe(III) hydroxides and $CaCO_3$ are responsible for a partial blockage of pore entrances of the zeolite pellets in case of the column operated with groundwater. Thus, we conclude that groundwater should be pre-treated by iron-removal and softening steps in order to exploit the performance of the zeolite optimally. A retardation of MTBE adsorption kinetics in river water (containing natural organic matter (NOM)) compared to its adsorption from ultrapure laboratory water has also been described in (19). These effects will depend on the specific water which has to be treated and must be considered in the design of large-scale adsorbers.

Comparison of Continuous and Intermittent Operation Modes for Wet Peroxide Oxidation with Fe-Zeolite Catalysts

A comparison of the main influencing factors of the two possible operation modes for wet peroxide oxidation with Fe-zeolites is shown in Table 3. Generally, the continuous mode can be considered as more demanding with regard to the necessary catalyst performance and process

TABLE 3

Comparison of the main influencing factors for the two possible operation modes of wet peroxide oxidation of contaminants in water using Fe-zeolite catalysts

	Continuous mode	Intermittent mode
Setup scheme		
H_2O_2 addition, consumption	Continuously at the reactor inflow, high consumption	Only within regeneration cycles, moderate consumption
Reaction conditions (e.g., pH, T)	Should be close to conditions of the water stream to be treated	Adjustable within a wider range
Reactor dimension (investment costs)	Determined by performance of Fe-zeolite as adsorber and catalyst for degradation of contaminants and all undesired oxidation intermediates	Determined mainly by performance of Fe-zeolite as adsorber for original contaminants

optimization. The necessary reactor residence time of the water, and thus the reactor size, is in this case determined by the adsorption properties and the reaction rates of the target contaminants and all undesired oxidation intermediates. Adsorption of the contaminant on the zeolite will retard its transport through the reactor relative to the water flow, i.e., increase its residence time. However, the residence time available for further degradation of the intermediates is determined by their own adsorption properties.

In contrast, in the intermittent mode, efficient adsorption of the contaminant will prolong the adsorption intervals and thus the available time for contaminant mineralization in the adsorber, which is later oxidatively regenerated. A further advantage of the intermittent mode can be seen in the fact that the conditions for the adsorption and oxidation steps can be adjusted independently. This allows, for instance, adjustment to more severe reaction conditions since a much lower volume has to be manipulated.

CONCLUSIONS

The Fe-zeolites studied are promising catalysts for the oxidative degradation of organic contaminants in water using H_2O_2 at near-neutral pH. Adsorption of the contaminants by the Fe-zeolite has a positive effect on the efficiency of their degradation with H_2O_2. Based on the specific adsorption affinities of the two Fe-zeolites under study, Fe-ZSM5 appears to be the optimal adsorber/catalyst for TCE while Fe-Beta is better suited for MTBE. The tested Fe-zeolites proved to be sufficiently stable, justifying further advanced testing for an application in flow-through, fixed-bed reactors. Suitable pre-treatment of the water (e.g., iron-removal and softening for groundwater), together with the application of regeneration options such as exhaustive oxidation of residues and renewal of the iron content of the zeolite still need to be tested in order to prolong the lifetime of these catalysts.

ACKNOWLEDGEMENTS

We thank Dr. R. Kurzhals (Süd-Chemie Zeolites, Bitterfeld, Germany) for providing the Fe-zeolites. Furthermore, we would like to thank Marion Hoyer for excellent technical assistance. Peter Morgenstern (Department of Analytical Chemistry, UFZ) is acknowledged for contributing the X-ray analysis of the zeolites. This work was supported by PIEF-GA-2009–236583 (EU Marie Curie Fellowship, R. Gonzalez-Olmos).

REFERENCES

1. Matta, R.; Hanna, K.; Kone, T.; Chiron, S. (2008) Oxidation of 2,4,6-trinitrotoluene in the presence of different iron-bearing minerals at neutral pH. *Chem. Eng. J.*, 144 (3): 453–458.
2. Phu, N.H.; Hoa, T.T.K.; Van Tan, N.; Thang, H.V.; Le Ha, P. (2001) Characterization and activity of Fe-ZSM-5 catalysts for the total oxidation of phenol in aqueous solutions. *Appl. Catal., B*, 34 (4): 267–275.
3. Kusic, H.; Koprivanac, N.; Selanec, I. (2006) Fe-exchanged zeolite as the effective heterogeneous Fenton-type catalyst for the organic pollutant minimization: UV irradiation assistance. *Chemosphere*, 65 (1): 65–73.
4. Melero, J.A.; Calleja, G.; Martinez, F.; Molina, R.; Pariente, M.I. (2007) Nanocomposite Fe_2O_3/SBA-15: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions. *Chem. Eng. J.*, 131 (1–3): 245–256.
5. Maletzky, P.; Bauer, R.; Lahnsteiner, J.; Pouresmael, B. (1999) Immobilisation of iron ions on Nafion® and its applicability to the Photo-Fenton method. *Chemosphere*, 38 (10): 2315–2325.
6. Gonzalez-Olmos, R.; Roland, U.; Toufar, H.; Kopinke, F.D.; Georgi, A. (2009) Fe-zeolites as catalysts for chemical oxidation of MTBE in water with H_2O_2. *Appl. Catal., B*, 89 (3–4): 356–364.
7. Doocey, D.J.; Sharratt, P.N.; Cundy, C.S.; Plaisted, R.J. (2004) Zeolite-mediated advanced oxidation of model chlorinated phenolic aqueous waste - Part 2: Solid phase catalysis. *Process Saf. Environ. Prot.*, 82 (B5): 359–364.
8. Kuznetsova, E.V.; Savinov, E.N.; Vostrikova, L.A.; Parmon, V.N. (2004) Heterogeneous catalysis in the Fenton-type system FeZSM-5/H_2O_2. *Appl. Catal., B*, 51 (3): 165–170.
9. Martinez, F.; Melero, J.A.; Botas, J.A.; Pariente, M.I.; Molina, R. (2007) Treatment of phenolic effluents by catalytic wet hydrogen peroxide oxidation over Fe_2O_3/SBA-15 extruded catalyst in a fixed-bed reactor. *Ind. Eng. Chem. Res.*, 46 (13): 4396–4405.
10. Melero, J.A.; Martínez, F.; Botas, J.A.; Molina, R.; Pariente, M.I. (2009) Heterogeneous catalytic wet peroxide oxidation systems for the treatment of an industrial pharmaceutical wastewater. *Water Res.*, 43 (16): 4010–4018.
11. Botas, J.A.; Melero, J.A.; Martinez, F.; Pariente, M.I. (2010) Assessment of Fe_2O_3/SiO_2 catalysts for the continuous treatment of phenol aqueous solutions in a fixed bed reactor. *Catalysis Today*, 149 (3–4): 334–340.
12. Quinlivan, P.A.; Li, L.; Knappe, D.R.U. (2005) Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter. *Water Res.*, 39 (8): 1663–1673.
13. Szostak, R. (1992) *Handbook of Molecular Sieves*; Van Nostrand Reinhold: New York.
14. Brunauer, S.; Deming, L.S.; Deming, W.S.; Teller, E. (1940) On a theory of the van der Waals adsorption of gases. *J. Am. Chem. Soc.*, 62: 1723–1732.
15. Pignatello, J.J.; Oliveros, E.; MacKay, A. (2006) Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology*, 36 (1): 1–84.
16. NDRL, Solution Kinetics Database, NDRL/NIST.
17. Burbano, A.A.; Dionysiou, D.D.; Suidan, M.T.; Richardson, T.L. (2005) Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent. *Water Res.*, 39 (1): 107–118.
18. Aguera, A.; Mezcua, M.; Hernando, D.; Malato, S.; Caceres, J.; Fernandez-Alba, A. (2004) Application of GC-MS and GC-AED to the evaluation of by-products formed by solar photo-fenton degradation of methyl tert-butyl ether in water. *Int. J. Env. Anal. Chem.*, 84 (1–3): 149–159.
19. Rossner, A.; Knappe, D.R.U. (2008) MTBE adsorption on alternative adsorbents and packed bed adsorber performance. *Water Res.*, 42 (8–9): 2287–2299.