Humic acid modified Fenton reagent for enhancement of the working pH range

A. Georgi, A. Schierz, U. Trommler, C.P. Horwitz, T.J. Collins, F.-D. Kopinke

Abstract

The suitability of the Fenton process for the remediation of soil and groundwater is limited by the necessity to acidify the reaction medium. This study examines the applicability of humic acid (HA) as an iron chelator in a modified Fenton system with the aim of extending the optimum pH range for this process towards neutral conditions. Addition of HA at a concentration of 50–100 mg L⁻¹ greatly enhances the rate of oxidation of organic compounds in a catalytic Fenton system in the range of pH 5–7. Similar rates at pH 5 in the presence of HA can be achieved as at pH 3 for a typical Fenton process in the absence of HA (k₀ = 9 × 10⁻³ min⁻¹ for benzene degradation at [H₂O₂] = 0.13 M). A comparison of the relative reactivities of various model compounds supported the hypothesis that OH radicals are the main reactive species in the HA-modified Fenton system. In contrast, however, another type of chelated Fe-catalyst (Fe-TAML) proved to be more selective than expected for OH radicals. A long-term study revealed that the HA itself is oxidized and thereby loses its ability to enhance the degradation of the pollutant molecules. Therefore, the HA-modified Fenton system is effective for degrading pollutants which are at least as reactive towards OH radicals as the HA itself, such as BTEX, phenols or PAHs. The results obtained indicate that the HA-modified Fenton system is also applicable for compounds with a high sorption tendency towards HA.

1. Introduction

Oxidation processes that involve the production of the highly reactive hydroxyl radical (OH⁺) are of current interest for the destruction of organic pollutants in surface and groundwaters as well as industrial wastewaters. The Fenton reagent, consisting of H₂O₂ and ferrous iron, has been shown to be effective in the degradation of a wide spectrum of organic and inorganic pollutants [1,2]. The hypothesis of Haber and Weiss [3] that the Fenton reaction involves the formation of OH⁺ radicals as the actual oxidants (Eq. (1)) is widely accepted. However, the participation of high-valent iron-oxo species has also been discussed, especially for systems where the iron is complexed [4,5]. The general mechanism for a free radical chain involves the following key steps:

1. H₂O₂ + Fe(II) → Fe(III) + HO⁺ + OH⁻
2. H₂O₂ + Fe(III) → Fe(II) + HO₂⁺ + H⁺
3. OH⁺ + H₂O₂ → HO₂⁺ + H₂O
4. OH⁺ + Fe(II) → Fe(III) + OH⁻
5. Fe(III) + HO₂⁺ → Fe(II) + O₂ + H⁺
6. Fe(II) + HO₂⁺ + H⁺ → Fe(III) + H₂O₂
7. HO₂⁺ + HO₂⁺ → H₂O₂ + O₂

Fe(II) and Fe(III) are representative for all species present in solution in each respective oxidation state. The hydroxyl radical formed in reaction (1) can react with organic compounds by H abstraction or addition to alkenes, alkynes or aromatic rings. In technical applications, iron is usually used in much lower concentration than hydrogen peroxide (catalytic

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Fenton systems) in order to avoid the formation of large amounts of iron sludge. Furthermore, the scavenging of $\cdot OH$ by Fe(II) (Eq. (4)) is reduced when iron is applied in catalytic concentrations. Since the recycling of Fe(III)/Fe(II) by reaction (2) is several orders of magnitude slower than reaction (1), it is considered as the rate-limiting step of the reaction chain in catalytic Fenton systems. The pH optimum for Fenton oxidations is usually reported in the acidic range near pH 3 [2]. However, groundwater and soil may possess a high buffer capacity. Therefore, the necessity to acidify the reaction medium limits the applicability of the Fenton process in environmental technology.

The main reason for the low reactivity at circumneutral pH is the precipitation of Fe(III) as hydroxylhydroxides Fe$_2$O$_3\cdot$nH$_2$O which inhibits the recycling of Fe(III)/Fe(II). In order to keep the iron in solution, the use of synthetic chelators such as aminopolycarboxylates, polyhydroxy aromatics and N-heterocyclic carboxylates [6,7] in modified Fenton systems has been studied. Furthermore, macrocyclic iron-chelating agents such as porphyrins [8], phthalocyanines [9] and tetraamido-macrocyclic ligands (Fe-TAML catalyst [10]) have also been employed. Sun and Pignatello [6] suggested that a ligand may influence the reactivity of the complex in a modified Fenton system by at least three ways: (I) by ligand-field effects on the redox-properties of the metal, (II) by allowing for a labile coordination position on the metal for complexation of H$_2$O$_2$ and (III) by its competition with the substrate for reaction with the oxidant.

In this study the application of humic acid in a modified Fenton system is examined. Humic substances are ubiquitous natural macromolecules resulting from microbial and chemical transformations of organic debris. Humic substances are classified into humic and fulvic acid (HA and FA) as well as humin according to their solubility characteristics. Humic acids can be obtained at relatively low cost by alkaline extraction of peat, lignite or leonardite and thus are commercially available on a large scale. Humic and fulvic acids are known to form complexes with metal ions by binding to carboxylate, polyphenolic and nitrogen-containing sites [11]. Fe(III) and Cu(II) are the most preferentially bound metals.

Beside their function as iron chelators, further effects of humic substances in the Fenton system may result from their ability to act as a sorbent for hydrophobic organic compounds as well as from their own redox activity.

In a study by Voelker and Sulzberger [12], an increase in the rate of H$_2$O$_2$ degradation by the Fenton reaction was observed at pH 5 when FA was added, whereas the effect was negligible at pH 3. The authors concluded that Fe(II)–fulvate complexes formed at pH 5 are able to react more rapidly with H$_2$O$_2$ than Fe(II)–aquo complexes, leading to a higher rate of $\cdot OH$ production. An increase in the rate of $\cdot OH$ production with increasing concentrations of FA was also reported in [13] for a stoichiometric Fenton system at pH $\geq$ 4.5. Furthermore, Voelker and Sulzberger [12] showed in their study that FA acts as a reductant of Fe(III); this was ascribed to a binding of Fe(III) to quinone-type structures in the FA.

On the other hand, quinones have been shown to catalyze the Fenton oxidation of organic compounds by electron shuttling. A redox cycle has been postulated [14,15] in which Fe(III) is reduced to Fe(II) by hydroquinone or a semiquinone radical, by-passing the slow step of the Fenton reaction (Eq. (2)). The resulting quinone can rapidly react with HO$_2^*$ generated by reaction (2), finally leading to the regeneration of hydroquinone [14,15]. The quinoid structures of humic substances are known to play an important role as electron shuttles in microbial redox reactions [16]. Based on this knowledge, a positive effect of the redox-active sites of humic substances on the recycling of Fe(III)/Fe(II) in the Fenton degradation of organic pollutants could be hypothesised.

In the literature, different results regarding the influence of humic substances on pollutant degradation in Fenton systems have been reported. Li et al. [17] applied a catalytic Fenton reaction at pH 3. They reported a slight deceleration of the degradation of trinitrotoluene in the presence of HA (40 mg C L$^{-1}$) whereas FA at 20 mg C L$^{-1}$ appeared to slightly promote the reaction.

Lindsey and Tarr [13] found a decrease in the rate of degradation of various aromatic compounds by the Fenton reaction (pH 2.5) when fulvic or humic acid in the concentration range of 5–30 mg L$^{-1}$ was added. Continuous addition of H$_2$O$_2$ was applied in these experiments, leading to a steady-state $\cdot OH$ concentration. The experimental conditions are more comparable to a stoichiometric than to a catalytic scenario. The fact that the steady-state $\cdot OH$ concentration was not influenced by the presence of FA suggests that $\cdot OH$ quenching by FA was insignificant in this system. The extent of deceleration was at least partly correlated with the hydrophobicity of the substrates. Therefore, the authors concluded that partitioning into the hydrophobic domains of humic substances is a key factor in the observed decrease in reactivity. The underlying mechanism was hypothesised to be a spatial separation between the iron-binding sites located within the hydrophilic regions of humic substances and the hydrophobic regions responsible for the partitioning of hydrophobic compounds [13]. In contrast, a positive effect of sorption on the Fenton degradation of hydrophobic organic compounds was observed in the case of cyclodextrin additions [18]. This result was explained by formation of a ternary complex, organic substrate–cyclodextrin–Fe(II), resulting in the formation of $\cdot OH$ radicals in close proximity to the included substrate molecule [18].

The intention of the present study was to examine the applicability of leonardite HA as an iron chelator in a modified Fenton system with the aim of extending the optimum pH range for this process towards neutral conditions.

2. Materials and methods

2.1. Materials and general procedures

Benzene, toluene, methyl tert-butyl ether (MTBE), trichloroethene (TCE), 1,1,2,2-tetrachloroethane (TeCA), 2,4,5-trichlorophenol, naphthalene, fluoranthene, oxalic acid, ethylenediaminetetraacetate (EDTA) and nitrolotriacetic acid
Aldrich (Germany) and had a purity of ≥98%. The HA was obtained from Carl Roth GmbH (Karlsruhe, Germany) and was used without further purification. According to the specifications of the manufacturer it is produced by alkaline extraction of leonardite. A polymeric autoxidation product of hydroquinone was produced by passing a gentle stream of air through an alkaline solution (pH 11) of p-hydroquinone (c = 1 g L⁻¹) for a time period of 24 h. The reaction solution firstly turned rosewood-coloured and then dark brown. Afterwards the solution was adjusted to pH 2. The precipitate was isolated by filtration, washed with deionized water and dried. Autoxidation products of polyhydroxybenzenes are irregular polymers containing polyphenolic and quinoid structures that are bridged by carbon–carbon or ether bonds [19].

The molecular structure of the Fe-TAML activator applied (Fig. 1) corresponds to the general structure of Fe-TAML activators reported in [10].

A stock solution of Fe(III) (c_{Fe(III)} = 30 mM) was prepared by dissolving Fe(NO₃)₃·9H₂O in dilute H₂SO₄ (pH 3). A stock solution of Fe(II) (c_{Fe(II)} = 220 mM) was prepared analogously from FeCl₂·4H₂O.

HA solutions were prepared by dissolving the appropriate amount of HA in deionized water that was adjusted to pH 11 by adding 0.1 M NaOH. Afterwards, each solution was brought to the appropriate pH by adding 1 M or 0.2 M H₂SO₄.

Hydrogen peroxide concentrations were monitored by iodometric titration with 0.1 M Na₂S₂O₃ [20].

All experiments were conducted at room temperature (T = 23 ± 2 °C).

2.2. Catalytic Fenton reaction

All reactions were conducted using two-neck bottles (280 mL). One neck was capped with a Mininert® valve and was used for introducing reactant solutions as well as for headspace sampling. The second neck was capped with a screw cap having a Teflon-lined septum with a pre-cut opening, through which a pH electrode was introduced. The flasks were wrapped in black plastic foil. 250 mL of deionized water or of a solution of HA or another complexing agent (EDTA, oxalic acid, NTA or hydroquinone polymer) were filled into the reaction vessel. The solutions were adjusted to pH 3 by adding 0.2 M H₂SO₄, after which the appropriate amount of the Fe(III)-stock solution was added and the pH of the solution was adjusted to the desired value (pH 3, 5, 6 or 7) with 1 or 0.1 M NaOH as appropriate. The solution was then spiked with the organic compounds (2 mg L⁻¹ each of benzene, toluene, MTBE, TCE and 40 mg L⁻¹ of TeCA) and shaken overnight on a horizontal shaker. The reaction was started by adding the appropriate amount of H₂O₂ (30%, w/w). During the reaction, the pH of the solution was readjusted by adding 0.1 M NaOH repeatedly in order to maintain a nearly constant pH (deviations ≤ ±0.3 pH units). The concentration of the organic compounds was determined by manual headspace sampling and GC analysis.

The experiments with fluoranthene and naphthalene were performed analogously. In these cases, flasks with a volume of 1 L were used. 100 µL of a stock solution of both compounds in ethanol (c = 1 g L⁻¹ of each compound) was applied as a thin film on the glass walls of the flask. The solvent was allowed to evaporate. A small loss of naphthalene due to this procedure was accepted. Shortly afterwards, 1 L of the aqueous reaction solution (pH 3 or 5, c_{Fe(III)} = 30 µM, either with or without 100 mg L⁻¹ of HA) was added. The solution was shaken overnight on a horizontal shaker. The reaction was started by adding H₂O₂ at a concentration of 65 mM. After certain time periods, aliquots of the solution (25 mL) were removed and mixed with 1.25 g of Na₂S₂O₃ in order to stop the reaction. Afterwards, these aliquots were extracted with 1 mL n-hexane containing d₄-naphthalene and pyrene as internal standards (1 h extraction time). The extracts were analyzed by GC-MS in the SIM (selected ion monitoring) mode. In order to investigate the influence of the oxidation of the HA on its sorption potential, calibration was performed by extraction of an aqueous standard solution with the same pH and ionic strength but without HA under the same conditions.

Degradation experiments were conducted at least twice. Comparing the residual concentrations remaining after certain time periods of reaction, the deviations of the two single values from the mean value were ≤10% of the mean value.

2.3. Stoichiometric Fenton reaction

240 mL of deionized water was filled into 250 mL-flasks with screw caps and Teflon-lined septa. The pH of the solution was adjusted to pH 3 by adding 1 M H₂SO₄. The solution was

Fig. 1. Molecular structure of the applied Fe-TAML activator.
purged with nitrogen for 30 min. Afterwards, 0.96 mL of an aqueous stock solution containing a mixture of the model compounds (500 mg L⁻¹ each of benzene, toluene, MTBE, TCE) was added. The flasks were wrapped in black plastic foil. Immediately after addition of 1.2 mL of the 0.22 M Fe(II)-stock solution, the reaction was started by adding 1.2 mL of a 0.22 M H₂O₂ stock solution. After a reaction period of 1 min the reaction was stopped by adding 0.24 mL of a 3 M Na₂S₂O₃ solution. The residual concentrations of the model compounds were determined by manual headspace sampling and GC analysis. Five replicate experiments were conducted.

2.4. Experiments with the iron-tetraamidomacrocyclic ligand complex

The Fe-TAML activator and H₂O₂ were added to a solution of 5 mM 2,4,5-trichlorophenol and 5 mM benzene in pH 10 buffer (100 mL, 0.1 M NaHCO₃/0.1 M Na₂CO₃) so that the final concentrations in the solution were 2.5 μM catalyst and 500 mM H₂O₂. The catalyst was added in two equal portions over 2 min, and the H₂O₂ was added in five equal portions over 4 min. The concentration of benzene was determined by headspace sampling followed by GC analysis. For the analysis of trichlorophenol, aliquots (10 mL) of the reaction solution were removed after 6, 7 and 9 min of reaction and filled into vials which contained 1 g of Na₂S₂O₃ in order to stop the reaction. Afterwards, the aliquots were brought to pH 5 by adding H₂SO₄ and extracted with n-hexane containing chlorobenzene as an internal standard. The extracts were analyzed by GC-MS in the SIM mode. The experiment at pH 10 was performed three times. Further experiments were conducted under variation of the pH in the range of pH 7–10.

3. Results and discussion

3.1. Variation of the reaction conditions (solution pH and concentrations of Fe(III), H₂O₂ and HA)

All reaction solutions initially received Fe(III) and H₂O₂ with c_{Fe(III),0} ≪ c_{H₂O₂,0}. Therefore, the reduction of Fe(III) is expected to be the rate-limiting step for the production of OH⁺ throughout the whole course of the reaction. The consumption of H₂O₂ was slow under all reaction conditions tested. Within a reaction period of 8 h depletion of H₂O₂ was ≤10% in most experiments.

The degradation rates of the various model compounds (benzene, toluene, MTBE, TCE, TeCA) applied showed a similar response to the variation of the reaction conditions. For the sake of clarity the effects are depicted exemplarily for benzene. Fig. 2a and b show the influence of the solution pH on the Fenton oxidation of benzene in aqueous solution with and without addition of HA, respectively. Preliminary experiments without continuous pH adjustment showed a considerable decrease in pH for the reaction solutions with an initial pH of 5–7. In order to keep the pH of the reaction solutions nearly constant, dilute NaOH was added in a stepwise manner.

As can be seen from Fig. 2a the rate of the reaction decreases significantly with increasing pH in the catalytic Fenton system without HA. This is in accordance with literature values for the optimum pH of the Fenton oxidation of organic compounds which mostly fall in the range of pH 2.5–3.5 [6,23,24]. In the solutions with pH 5–7 a precipitation of Fe(III), presumably as hydrous oxyhydroxides Fe₂O₃·nH₂O, was observed. In contrast, no precipitation occurred in reaction solutions containing 30 μM Fe(III) and HA at concentrations of 10–100 mg L⁻¹. Fig. 2b shows the kinetics of the degradation of benzene in the presence of HA with all other reaction conditions comparable to the experiment presented in Fig. 2a. At pH 3 the rate of the reaction is not significantly influenced by the presence of HA. Benzene degradation followed a pseudo-first-order kinetics in HA-free and HA-containing solution at pH 3. The pseudo-first-order rate constants were not significantly different in both systems (without HA: k’ = (9.0 ± 0.9) × 10⁻³ min⁻¹, with HA: k’ₕₐ = (12 ± 2.0) × 10⁻³ min⁻¹). This result is in accordance with the rather low effects exerted by additions of HA and FA on the degradation of trinitrotoluene in a catalytic Fenton system at pH 3 as reported in [17]. However, at pH 5, 6 and 7 benzene degradation is significantly accelerated by the presence of HA. Obviously, at a pH range of 5–7 the leonardite HA forms soluble complexes with iron that are able to activate H₂O₂. While benzene degradation in the HA-modified Fenton system is comparably fast at pH 3 and 5, it is decelerated when

![Fig. 2. Influence of pH on the degradation of benzene in a catalytic Fenton system (a) without HA and (b) with addition of 50 mg L⁻¹ HA (c_{Fe(III),0} = 30 μM, c_{H₂O₂,0} = 130 mM, c_{benzene,0} = 25 mM), symbols: △, pH 3; □, pH 5; ×, pH 6; ▲, pH 7.](image-url)
the pH of the solution is further increased (Fig. 2b). However, when the reaction in HA-containing solution was started at pH 7 without continuous pH adjustment, after 24 h of reaction the pH value had decreased spontaneously to pH 3.7 due to the formation of acidic oxidation products. 95% degradation of benzene was reached after a reaction period of 6 h and ≥99% after 24 h.

In HA-containing as well as HA-free solutions above pH 3, deviations from pseudo-first-order kinetics were observed that were more distinct with increasing pH. Deviations from pseudo-first-order kinetics such as the occurrence of lag periods at the start of the reaction or a deceleration of the reaction are often observed in Fenton reaction systems. These effects have been ascribed to the intervention of intermediate oxidation products in the Fenton reaction. On the one hand, oxidation products that are able to complex Fe(III)/Fe(II) can be formed. This complexation can positively or negatively affect Fe(III)/Fe(II) recycling as well as the rate of OH* formation [7,15,24]. Furthermore, the occurrence of intermediate oxidation products that are able to reduce Fe(III) faster than H₂O₂ can be a reason for a turnover-dependent acceleration of the reaction [14].

The strongest positive effect of HA is observed at pH 5. In HA-containing solution the reaction rate at pH 5 is comparable to that at pH 3 (Fig. 2b). Therefore, in further experiments the influence of the initial concentrations of Fe(III), HA and H₂O₂ on the reaction rate at this pH was studied.

The influence of the initial concentrations of Fe(III) and H₂O₂ on the rate of benzene degradation in the presence of 50 mg L⁻¹ HA is shown in Table 1. The rate of the reaction in the various systems was compared on the basis of the reaction time needed for 95% degradation of benzene. When only HA and H₂O₂ or Fe(III) and HA were added to the reaction solutions, no significant degradation of benzene was observed within 24 h. The reaction rate increased with increasing concentrations of Fe(III) and H₂O₂. The highest applicable concentration of Fe(III) at a HA concentration of 50 mg L⁻¹ was 90 μM at pH 5. A concentration of 100 μM resulted in a flocculation of the HA, probably as a result of charge neutralization and intermolecular bridging of HA molecules. The applied HA has a content of carboxylic and phenolic hydroxyl groups of 3.4 and 2.0 mmol g⁻¹ [25], respectively. At a Fe(III)/HA concentration ratio of 90 μM/50 mg L⁻¹, about 70% of the total acidic groups of the HA might be involved in iron complexation if bidentate complexes are assumed. However, it is possible to prepare even more concentrated solutions of Fe(III) and HA for later dilution. At a HA concentration of 500 mg L⁻¹ at pH 7, solutions are stable up to 1 mM Fe(III).

Since H₂O₂ itself acts as a quencher of OH* (Eq. (3)), most studies report the existence of an optimum H₂O₂ concentration for the degradation of organic compounds by means of the catalytic Fenton process. A similar effect is observed in this study since benzene degradation is not further accelerated when c₃H₂O₂₀ is increased from 65 to 130 mM (Table 1b). Summing up the data in Table 1, the range of observed reaction rates is rather narrow, differing by less than a factor of two.

Fig. 3 shows the influence of the HA concentration on the rate of benzene degradation. At a HA concentration of 10 mg L⁻¹ after passing a lag phase the reaction becomes faster than without addition of HA. A HA concentration of 10 mg L⁻¹ was already sufficient to keep the iron in solution. On the other hand the positive effect of HA on the oxidation reaction increased with increasing HA concentration, i.e. the lag phase was shortened and ≥95% turnover of benzene are observed within a reaction period of 5 h in the presence of 50 or 100 mg L⁻¹ HA compared with about 35% turnover in HA-free solution. The reduction of Fe(III) is considered as the rate-limiting step for the production of OH* in catalytic Fenton systems. Therefore, it is plausible that the HA-induced increase in the rate of benzene degradation that we observed in our experiments results from the acceleration of Fe(III) reduction. Changes in the rate of the reaction of Fe(II) and H₂O₂ (Eq. (1)) due to the formation of Fe(II)–HA complexes would only become important for catalytic Fenton systems in case of strong inhibiting effects. However, Voelker and Sulzberger [12] reported an accelerating effect of FA on reaction (1).

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**Table 1**

<table>
<thead>
<tr>
<th>(a) c₃Fe(III)₀ (μM) at c₃H₂O₂₀ = 65 mM</th>
<th>t₀.95 (min)</th>
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<td>15</td>
<td>420</td>
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<td>90</td>
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<tr>
<th>(b) c₃H₂O₂₀ (mM) at c₃Fe(III)₀ = 30 μM</th>
<th>t₀.95 (min)</th>
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<tr>
<td>13</td>
<td>≥400</td>
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<tr>
<td>65</td>
<td>300</td>
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<td>130</td>
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![Fig. 3](attachment:Fig_3.png)

Fig. 3. Influence of the initial HA concentration on the degradation of benzene in the HA-modified Fenton system (pH 5, c₃H₂O₂₀ = 65 mM, c₃Fe(III)₀ = 30 μM, c₃benzene₀ = 25 μM), symbols: Δ, 0 mg L⁻¹ HA; ×, 10 mg L⁻¹ HA; ▲, 50 mg L⁻¹ HA; , 100 mg L⁻¹ HA.
The accelerating effect that increasing HA concentrations exert on substrate degradation in the HA-modified Fenton system can have several reasons. Firstly, different types of Fe(III)–HA complexes can be formed depending on the concentration ratio of iron and HA in the solution. This is due to the competition of different functional groups of the HA in the binding of iron. An increase in HA concentration can be accompanied with a shift in responsible binding sites towards those with higher stability constants. If these sites simultaneously facilitate Fe(III) reduction the reaction would be accelerated with increasing HA concentration until all of the Fe(III) is bound to this type of sites. Furthermore, in case of a direct participation of redox-active sites of the HA in the reduction of Fe(III), the rate of this reaction would be directly related to HA concentration.

On the other hand, the quenching of OH\(^\cdot\) by HA has to be considered. The relative rate of the reactions of OH\(^\cdot\) with each of the quenchers present in the system can be estimated according to the following equation:

\[
\frac{\nu_n}{\nu_m} = \frac{k_{n,\text{OH}^\cdot} c_n}{k_{m,\text{OH}^\cdot} c_m}
\]

where \(\nu_n\) and \(\nu_m\) are the rates of the reactions of the species \(n\) and \(m\) with OH\(^\cdot\), \(k_{n,\text{OH}^\cdot}\) and \(k_{m,\text{OH}^\cdot}\) are the second-order-rate constants of these reactions and \(c_n\) and \(c_m\) are the local concentrations of these species in the environment of the OH\(^\cdot\) radicals. Due to the complexation of Fe(II) and Fe(III) by the HA these concentrations are not necessarily identical to the bulk phase concentrations since the travel distance of OH\(^\cdot\) radicals is only some tenth of nm. Relevant quenchers in our reaction solutions are H\(_2\)O\(_2\) (\(k_{\text{H}_2\text{O}_2,\text{OH}^\cdot} = 2.7 \times 10^7 \text{ M}^{-1} \text{s}^{-1}\) [26]) and HA. Brezonik and Fulkerson-Breken [27] have reported an average value of \(1.7 \times 10^4 \text{ L (mg C)}^{-1} \text{s}^{-1}\) (corresponding to \(2.0 \times 10^5 \text{ L (mol C)}^{-1} \text{s}^{-1}\) for the second-order-rate constant for reaction with OH\(^\cdot\) for several aquatic humic substances. Using this value as an approximate value for the HA applied in this study, we can estimate that in the solutions containing 65 mM H\(_2\)O\(_2\) the quenching of OH\(^\cdot\) by HA is negligible compared to that by H\(_2\)O\(_2\) when the HA concentration is low (\(\nu_{\text{H}_2\text{O}_2}/\nu_{\text{DOC}} \approx 20\) at \(c_{\text{HA}} = 10 \text{ mg L}^{-1}\)), whereas the quenching ratio increases to values of \(\nu_{\text{H}_2\text{O}_2}/\nu_{\text{DOC}} \approx 4\) and 2 at HA concentrations of 50 or 100 mg L\(^{-1}\), respectively. Consequently, higher concentrations of HA would result in a significant quenching effect of OH\(^\cdot\) radicals by HA. The close proximity of OH\(^\cdot\) generation sites and HA structures responsible for OH\(^\cdot\) quenching possibly leads to an underestimation of the assumed quenching effect of HA. Actually, the increasing quenching effect of HA might be a reason for the rather low increase in reactivity that is observed after increasing the HA concentration from 50 to 100 mg L\(^{-1}\). Obviously, there is an optimum concentration of HA for the system, since positive and negative effects of HA superimpose.

Summarizing the results of the experiments at varying reactant concentrations, the application of 30 \(\mu\text{M}\) Fe(III), 65 mM H\(_2\)O\(_2\) and 50 mg L\(^{-1}\) HA at \(\text{pH} 5\) can be considered as sufficient in order to achieve an acceptable degradation rate for benzene in a possible in situ chemical oxidation (ISCO) application.

### 3.2. Variation of the type of iron chelator

Sun and Pignatello [6] studied the influence of various polydentate organic ligands on the Fe(III)-catalyzed oxidation of 2,4-dichlorophenoxyacetic acid (2,4-D) with H\(_2\)O\(_2\) at \(\text{pH} 6\). Despite the large number of different ligands applied, such as aminopolycarboxylates, polycarboxylates, polyhydroxy aromatics and N-heterocyclic carboxylates, a clear structure–activity correlation could not be derived. With respect to their catalytic activity the various ligands were classified into inactive or showing low, moderate and high activity, respectively. In order to evaluate the magnitude of the promoting activity of HA, several ligands that were applied in the study by Sun and Pignatello [6] were used in parallel experiments under the same conditions as HA. Furthermore, a polymeric autoxidation product of hydroquinone was applied as a macromolecule that is humic-like but bears predominantly phenolic OH-groups. Fig. 4 shows the kinetics of benzene oxidation in the experiments with the various ligands. Within the whole reaction period of about 6 h no formation of precipitates was observed (with the exception of pure aqueous solutions), suggesting that all of the ligands tested as well as their possible oxidation products were able to completely complex the Fe(III) present in the system. The Fe(III)–EDTA complex was inactive while the catalytic activity of the oxalic acid and NTA complexes in the oxidation of 2,4-D with H\(_2\)O\(_2\) at \(\text{pH} 6\) has been designated as low and high, respectively [6]. Qualitatively, this ranking was confirmed in our experiment. However, oxalic acid inhibited the reaction compared to the aqueous solution without addition of any ligand at \(\text{pH} 5\). The polymer resulting from autoxidation of hydroquinone was only moderately active. Similar to the behaviour of catechol in the study of Sun and Pignatello [6] it became more active after a lag phase, probably due to the fact that it has been oxidized itself.
However, humic acid showed by far the highest activity, even higher than NTA that was designated as highly active in [6]. Another promising type of activators for H$_2$O$_2$ consists of the iron-complexes with tetraamidomacrocyclic ligands (Fe-TAML catalysts). It has been reported that with this type of catalysts, deep oxidation of chlorophenols is reached within $\leq$10 min at alkaline pH [10]. We applied a Fe-TAML catalyst following the experimental procedure described in [10] in a solution containing 2,4,5-trichlorophenol (pK_a = 6.94 [28]) and benzene at pH 10. In accordance to the results described in [10], we observed a rapid degradation of the chlorophenol (Fig. 5). However, the reaction of benzene proceeded at a much lower rate. A variation of the pH of the reaction solution between pH 7–10 did not significantly improve the rate of benzene degradation. The rate constants for the reaction of chlorophenolate and benzene with OH$^*$ would normally be expected to be in the same order of magnitude (e.g. $k_{\text{pentachlorophenolate,OH}^*} = 1.1-3.7 \times 10^8$ M$^{-1}$ s$^{-1}$, $k_{\text{benzene,OH}^*} = 8 \times 10^7$ M$^{-1}$ s$^{-1}$ [26]). Therefore, the vastly different reactivity of these two compounds indicates that a reactive species other than OH$^*$ is responsible for the fast oxidation of chlorophenols in the Fe-TAML system. Obviously, this species is much more selective in its reactivity towards organic compounds than OH$^*$ radicals. In [29] high-valent iron-oxo complexes are suggested as the oxidative entity in Fe-TAML catalysts.

### 3.3. Stability of the HA-modified Fenton system

A further relevant property of a suitable iron chelator is its stability. Sun and Pignatello [6] noted that virtually all of the ligands investigated in their study were oxidized themselves. Self-oxidation was also reported for the Fe-TAML catalysts [10]. From the literature it is known that humic substances react with OH$^*$ resulting in bleaching, mineralization and production of low-molecular-weight acids such as formic, acetic, malonic and oxalic acid [30]. In the HA-modified Fenton system the original brown colour of the HA solution turned into yellow during the reaction. In order to study the degradation of the HA, a typical reaction system (pH 5, 30 $\mu$M Fe(III), 65 mM H$_2$O$_2$ and 100 mg L$^{-1}$ HA) without organic contaminants was investigated. An inspection of the UV/Vis spectra of the solution before and after the reaction revealed a decrease in the specific absorptivity over the whole wavelength range investigated (270–450 nm), pointing to a destruction of aromatic rings, conjugated double-bonds and other chromophores of the HA. Furthermore, the ratio of the absorption in the UV (280 nm) and visible range (440 nm), $E_{280}/E_{440}$, increased from 3.8 beforehand to 13.1 after a reaction period of 24 h. The ratio of the absorption in the ranges of 250–280 and 440–470 nm (e.g. $E_{250}/E_{465}$, $E_{280}/E_{440}$) has been shown to decrease with increasing molecular weight of natural humic substances (e.g. [31]). Correspondingly, the increase in $E_{280}/E_{440}$ is an indication for the fragmentation of macromolecules into smaller units.

The concentration of dissolved organic carbon (DOC) in the solution was initially 49 mg L$^{-1}$. After a reaction period of 8 h the concentration of dissolved carbon (DC) was 42 mg L$^{-1}$. After acidification of the solution (pH 3) and purging with nitrogen for 30 min the DC concentration had decreased to 28 mg L$^{-1}$. That means about 43% of the humic acid carbon were transformed into (under acidic conditions) volatile compounds. The main part of this fraction should be carbon dioxide since the Henry’s law coefficients of other oxidation products such as organic acids are rather low. These results point to a drastic change of the humic acid structure due to oxidation reactions including the formation of easily water soluble products, e.g. FA-like structures up to partial mineralization of the HA. ISCO processes in general involve the formation of oxidation products of humic substances resulting from side reactions with soil or sediment organic matter. Oxidation of humic substances by OH$^*$ is a natural process occurring in surface waters due to photochemical production of OH$^*$ and is thought to increase the bioavailability of terrestrially derived humic material [32]. Advanced oxidation processes such as the Fenton process have even been suggested for the destruction of natural organic matter (including humic substances) within the process of drinking-water purification [33]. Therefore, in our opinion the formation of oxidation products of HA during a remediation application of a modified Fenton system involving HA as iron chelator will not have to be considered as an ecotoxicological risk.

In order to investigate the effect of the oxidation of the HA on their ability to act as a promoter in the modified Fenton reaction, an experiment (pH 5, 30 $\mu$M Fe(III), 65 mM H$_2$O$_2$ and 50 mg L$^{-1}$ HA) with recurrent additions of benzene was conducted (Table 2). Within the first 5 h of reaction (phase 1) benzene was degraded by 95%. After a reaction period of 24 h the second addition of benzene was performed (start of phase 2). At this point the concentration of H$_2$O$_2$ was still $\geq$85% of its initial value. No precipitation was observed within phase 2, i.e. the oxidation products of the HA are still able to complex Fe(III). However, the oxidized HA was not able anymore to accelerate the degradation of benzene. The reaction in phase 2 was comparably slow and was as incomplete as the reaction in water at pH 5 without addition of HA (26% turnover within 5 h). In order to test whether the system can be reactivated,
fresh HA (50 mg L\(^{-1}\)) was added together with benzene (25 \(\mu\)M) 48 h after starting the experiment (start of phase 3). The degradation of benzene within phase 3 occurs at a rate that is intermediate to those of phase 1 and 2 (44% turnover within 5 h). The concentration of \(\text{H}_2\text{O}_2\) at the start of phase 3 was still 80% of the initial concentration in phase 1. The fact that the reactivity of the system is only incompletely recovered by adding fresh HA can be interpreted as being due to competition between the unfavourable iron-complexation by the HA-oxidation products still present in the system and the favourable iron-complexation by the freshly added HA. A further addition of benzene (start of phase 4, 72 h after start of the experiment) again revealed a decrease in the reactivity of the system (only 23% turnover within 5 h).

The nonspecific high reactivity of OH\(^{\cdot}\) radicals that is beneficial for the degradation of organic pollutants is at the same time detrimental for the long-term stability of organic iron ligands in modified Fenton systems. In principle, the ligands must only function over the time needed to reach a sufficient degradation of the pollutant. Therefore, the HA-modified Fenton system is beneficial for pollutants which are at least as reactive towards OH\(^{\cdot}\) radicals as the HA itself, such as BTEX, phenols or PAHs.

From the point of view of catalyst stability against self-destruction, the tested Fe-TAML catalyst profits from its moderately reactive oxidizing species. Obviously, they are more selective than OH\(^{\cdot}\) radicals. However, their higher selectivity (lower reactivity) is a disadvantage with respect to the pattern of pollutants which potentially can be degraded.

### 3.4. Influence of sorption to HA on the degradation reaction

Lindsey and Tarr [13] reported that sorption of pollutant molecules to humic substances hinders their degradation by OH\(^{\cdot}\) radicals in Fenton systems. The underlying mechanism was hypothesised to be a spatial separation between the iron binding sites located within the hydrophilic regions of humic substances and the hydrophobic regions responsible for the partitioning of hydrophobic compounds. However, the extent of inhibition did not strictly follow the order of hydrophobicity of the substrates in their study. They monitored the reaction of the two PAHs phenanthrene and pyrene, which showed the strongest inhibition upon addition of the humic substances, by measuring the decay of fluorescence intensity over time. The fluorescence intensity of a sorbate in the presence of dissolved humic substances is proportional to the concentration of the freely dissolved sorbate fraction. However, it is necessary to correct the raw data for the inner-filter effect and the fluorescence intensity caused by the presence of humic substances [34,35]. No information is given about the implementation of these corrections in [13]. Due to the oxidation of the humic substances, their sorption properties as well as their UV absorptivity and fluorescence intensity will change during the reaction. Therefore, it seems questionable whether the interpretation of fluorescence data is appropriate in this case.

In the present study the reaction rates of two hydrophobic compounds, naphthalene and fluoranthene, which differ greatly in their sorption potential on HA, have been compared. Solvent extraction followed by GC-MS analysis was applied as the analytical method for measuring total substrate concentrations. Fig. 6a shows the degradation kinetics of both compounds in a catalytic Fenton system at pH 3 and 5 without the addition of HA. Neither compound was significantly degraded in the solutions at pH 5; both showed a comparable reactivity at pH 3. As Fig. 6b shows, in the HA-containing solution at pH 5, fluoranthene is degraded at the same rate as naphthalene, at least within the first 4 h of reaction.

The sorbed fractions of both PAHs were determined by SPME in independent batch experiments. At a HA concentration of 100 mg L\(^{-1}\) at pH 5 fluoranthene is sorbed to the applied HA by a fraction of 88% (log \(K_{\text{DOM}} = 4.9\)) whereas naphthalene is sorbed by a fraction of only 9% (log \(K_{\text{DOM}} = 3.0\)). Due to the oxidation of the HA its sorption potential is expected to decrease. The sorbed fraction of fluoranthene after a reaction period of 1 h was still nearly the same as at the start of the reaction. However, it had decreased from initially 88% to a value of 26% after 4 h of reaction. Within the initial phase of the reaction, when the sorption potential of the HA was highest, no discrimination between the reactivity of naphthalene and fluoranthene was observed, despite of their different extents of sorption. Due to complexation, Fe(III) and Fe(II) are concentrated in the microenvironment of the HA. This results in a higher rate of OH\(^{\cdot}\) production in the microenvironment of the HA compared with the bulk aqueous solution. On the other hand, the concentration of molecular structures that are able to quench OH\(^{\cdot}\) is higher within the microenvironment of the HA than in the bulk phase. Possibly, positive and negative effects of sorption on the oxidation rates may compensate each other.

Our results are in contrast to the findings of Lindsey and Tarr [13] who reported an overall inhibiting effect of sorption to dissolved HA on the Fenton oxidation of hydrophobic compounds at pH 2.5. Apparently, it is possible that sorption

### Table 2

Benzene degradation in a long-term experiment with sequential additions of benzene (each 2 mg L\(^{-1}\)) and HA (each 50 mg L\(^{-1}\)), \(c_{\text{Fe(III)}} = 30 \, \mu\)M, \(c_{\text{H}_2\text{O}_2} = 65 \, \text{mM}, \text{pH} \ 5\)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Time elapsed at start of phase (h)</th>
<th>Reactants added at start of phase</th>
<th>(c_{\text{H}_2\text{O}<em>2}/c</em>{\text{H}_2\text{O}_2,0}) at start of phase (%)</th>
<th>Benzene turnover within a reaction period of 5 h (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>Benzene, HA, Fe(III), H(_2)O(_2)</td>
<td>100</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>Benzene</td>
<td>88</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>48</td>
<td>Benzene, HA</td>
<td>78</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>72</td>
<td>Benzene</td>
<td>70</td>
<td>23</td>
</tr>
</tbody>
</table>
to HA can exert either an accelerating or an inhibiting effect on the Fenton oxidation of hydrophobic pollutants depending on the respective reaction conditions.

Irrespective of the mechanistic interpretation, our results clearly show that with the HA-modified Fenton system (pH 5) under optimal conditions, degradation of hydrophobic pollutants with a high sorption potential is possible.

3.5. Selectivity of the degradation reaction in the HA-modified Fenton system

In order to study the selectivity of the oxidation reaction in the HA-modified Fenton system, a cocktail of structurally different compounds (TeCA, MTBE, TCE, benzene, toluene) was applied. While toluene and benzene were nearly completely degraded within a reaction period of 8 h in the HA-modified Fenton system, the degradation of MTBE and TCE proceeded at a considerably slower rate (Table 3). In the case of TeCA, no significant degradation was observed within 8 h of reaction.

From the selectivity of a reaction, information on the nature of the reactive species can be derived. Therefore, the relative rate constants of the various compounds with respect to the rate constant of benzene were determined. The rate of the reaction of a substrate $i$ with a given reactive species is determined by the following rate law:

$$\frac{dc_i}{dt} = -k_i c_r c_i$$

with $c_r$ and $c_i$ being the concentrations of the reactive species (e.g. OH$^-$ radicals) and the substrate, respectively.

For the parallel reaction of two compounds $n$ and $m$ with a certain reactive species Eq. (10) can be established which is transformed by integration into Eq. (11). Consequently, the relative rate constant $k_n/k_m$ can be easily derived from the residual concentrations ($c_n$ and $c_m$) of the two compounds at any point of time during the reaction (Eq. (11)).

$$\frac{dc_n}{dc_m} = \frac{k_n c_n}{k_m c_m}$$

$$\frac{k_n}{k_m} = \frac{\ln(c_n/c_n,0)}{\ln(c_m/c_m,0)}$$

This simplified derivation holds only for cases where one kind of reactive species dominates the attack on the hydrocarbon substrates. Otherwise, Eq. (9) comprises the
sum of several contributions ($\sum_i c_i R_i$) with $R$ as the index of the reactive species) where the variable concentrations $c_R$ cannot be cancelled out. Table 3 shows the relative rate constants of the various compounds in the HA-modified Fenton system with benzene as the reference. In order to test the hypothesis that OH* radicals are the reactive species in the modified Fenton system, the relative rate constants in this reaction system were compared with those in a stoichiometric Fenton system. Benzene, toluene and TCE were degraded by the HA-modified Fenton system, the relative rate constants in this Table 3 shows the relative rate constants obtained from the oxidation of this cocktail can be regarded as the fingerprint of the reactive oxidizing species. The fingerprint of those species responsible for oxidation in the HA-modified Fenton system (Table 3) is very similar to that of OH* radicals.

Methanol is known to be a strong quencher of OH* radicals ($k_{MCH,OH}* \approx 1 \times 10^8 M^{-1} s^{-1}$ [26]). The addition of 1% (v/v) methanol to the HA-modified Fenton system strongly inhibited the reaction of all model compounds. In conclusion, the results obtained are consistent with the hypothesis that OH* radicals are the dominant reactive species in the HA-modified Fenton system.

### 4. Summary and conclusions

Application of Leonardite HA is a promising means for extending the optimum pH of the catalytic Fenton process towards neutral conditions. At a HA concentration of 50–100 mg L$^{-1}$ the rate of benzene degradation by the catalytic Fenton reaction at pH 5 is as fast as at pH 3 without HA addition.

When the Fenton reaction is applied for in situ chemical oxidation of contaminants in groundwater, an acidic solution (pH 3) of Fe(II) and $H_2O_2$ is usually injected. Due to mixing with the groundwater, the pH of the injectate may increase, leading to a deceleration of contaminant degradation. In the case of a significant carbonate content in the groundwater, acid addition is even considered impractical. Addition of HA to the injection solution should increase the robustness of the catalytic system against neutralization of the reaction medium.

Furthermore, Fe(II) and Fe(III) are strongly exchanged on subsurface solids, leading to a potential loss of catalyst downgradient. Chelation of Fe(II)/(III) by HA might increase the migration distance of the catalyst. Taking into account the prices of $H_2O_2$ (about 650 €/t) and HA (about 1000 €/t of dry sodium humate) and the concentration ratio applied in the HA-modified Fenton system ($c_{H_2O_2} \geq 20 c_{HA}$), it becomes obvious that the addition of HA will only marginally increase the costs of a Fenton application.

However, due to the generation of nonselective OH* radicals the humic acid itself is oxidized and thus the modified Fenton system is deactivated slowly. This unavoidable phenomenon restricts the applicability of any organic oxidation catalyst which promotes the generation of OH* radicals. In contrast to the Fe–HA system, the tested Fe-TAML catalyst profits from a less reactive, more selective oxidizing species (possibly chelated high-valent iron), which may protect it from fast deactivation.

Further studies under conditions approaching those of in situ groundwater treatment will be conducted in order to prove the applicability of the HA-modified Fenton system for in situ chemical oxidation.

### References


