

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

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Received 12 July 2006; received in revised form 10 October 2006; accepted 16 October 2006

Available online 13 November 2006

## 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<sup>-1</sup> 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 ( $k' = 9 \times 10^{-3} \text{ min}^{-1}$  for benzene degradation at  $c_{\text{H}_2\text{O}_2} = 0.13 \text{ M}$ ). A comparison of the relative reactivities of various model compounds supported the hypothesis that OH<sup>•</sup> 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<sup>•</sup> 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<sup>•</sup> 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.

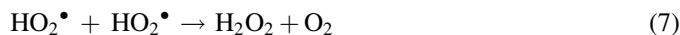
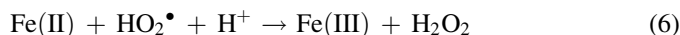
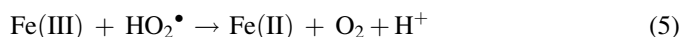
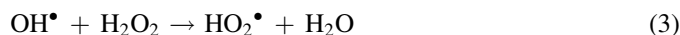
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**Keywords:** Hydrogen peroxide; Humic substances; Fenton; Iron chelators; AOP

## 1. Introduction

Oxidation processes that involve the production of the highly reactive hydroxyl radical (OH<sup>•</sup>) are of current interest for the destruction of organic pollutants in surface and groundwaters as well as industrial wastewaters. The Fenton reagent, consisting of H<sub>2</sub>O<sub>2</sub> 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<sup>•</sup> 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:



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  $\text{OH}^\bullet$  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 hydrous oxyhydroxides  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  than Fe(II)–aquo complexes, leading to a higher rate of  $\text{OH}^\bullet$  production. An increase in the rate of  $\text{OH}^\bullet$  production with increasing concentrations of FA was also reported in [13] for a stoichiometric Fenton system at  $\text{pH} \geq 4.5$ . 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  $\text{HO}_2^\bullet$  generated by reaction (2), finally leading to the regeneration of hydroquinone [14,15]. The quinoid structures in 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 ( $40 \text{ mg C L}^{-1}$ ) whereas FA at  $20 \text{ mg C L}^{-1}$  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  $5\text{--}30 \text{ mg L}^{-1}$  was added. Continuous addition of  $\text{H}_2\text{O}_2$  was applied in these experiments, leading to a steady-state  $\text{OH}^\bullet$  concentration. The experimental conditions are more comparable to a stoichiometric than to a catalytic scenario. The fact that the steady-state  $\text{OH}^\bullet$  concentration was not influenced by the presence of FA suggests that  $\text{OH}^\bullet$  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  $\text{OH}^\bullet$  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 nitrilotriacetic acid

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