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Effect of humic acids on the Fenton degradation of phenol

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Abstract We show that the degradation of phenol by Fe(III) and hydrogen peroxide is faster in the presence of humic acids. This is most likely due to faster reduction of Fe(III)-humate complexes by $\text{H}_2\text{O}_2/\text{HO}_2^-/\text{O}_2^{\cdot-}$ when compared with Fe(III)- H_2O complexes. The fact that humic acids, a major class of naturally occurring compounds, favour the Fenton reaction has great relevance in the field of water and soil decontamination, where organic compounds usually have a negative effect. Furthermore, it adds insight into the self-depuration processes of natural aquifers.

Keywords Water · Soil · Remediation · Advanced oxidation processes · Fe(II) · Fe(III) · Hydrogen peroxide · Natural waters · Natural organic matter · Pollutant degradation

Introduction

The presence of natural organic matter in water and soil has to be considered when applying remediation techniques aimed at pollutant removal. In the context of oxidative remediation processes, natural organic compounds occurring in water and in soil extracts are usually a problem because these compounds may act as scavengers of reactive species, e.g. hydroxyl radicals, thus protecting pollutants from degradation (Lindsey and Tarr 2000). Additionally, light absorption by organic compounds is likely to interfere with photochemical processes for water treatment. In some cases, irradiation of natural organic

compounds, acting as photosensitisers, e.g. humic acids (Boule et al. 1999), leads to photodegradation of pollutants. Also in this case, however, the photodegradation efficiency of natural matter is usually lower when compared with photochemical agents for water treatment, and competition for light absorption results in a decrease of the process efficiency. As a consequence, the level of interference of natural organic compounds on remediation processes is a factor to be considered in the choice of the remediation techniques.

Among the remediation techniques, the Fenton reaction is a promising process to thermally generate hydroxyl radicals (De Laat and Gallard 1999; Guivarch et al. 2003; Sanz et al. 2003):



Eq. 1 represents the first reaction of a series that involves all the species shown plus $\text{HO}_2^-/\text{O}_2^{\cdot-}$. Furthermore, the reaction shown in Eq. (1) is also the most controversial of all reactions involved in the Fenton process. It is likely to proceed via Fe-hydroperoxy complexes as reactive intermediates, and many authors have advanced the hypothesis that the Fenton reactivity is due to these species rather than to the hydroxyl radical, as discussed for instance by Bossmann et al. (1998).

The Fenton reaction is a promising technique for the remediation of contaminated soil extracts. In this context the evaluation of the effects of natural organic matter in general, and humic acids in particular, on the Fenton process is a major goal. So far, some information is available on the effects of fulvic acids in the reaction exemplified by Eq. (1), but unfortunately the existing data are not in agreement (Voelker and Sulzberger 1996; Lindsey and Tarr 2000). Humic and fulvic acids are the products of the oxidative degradation of organic material, and their reluctance to further transformation processes makes them very common in the environment (Boule et al. 1999).

Here we studied the effect of humic acids on the Fenton reaction. Furthermore, this investigation is also relevant to natural aquatic chemistry. Indeed, natural or-

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ganic matter can be both a source and a sink of hydroxyl radicals, the concentration of which in natural waters is influenced by both the nature and the concentration of dissolved organic compounds (Brezonik and Fulkerson-Brekken 1998). Considering that the Fenton reaction plays a relevant role in the iron redox cycling and in the oxidation processes taking place in natural aquifers (Voelker et al. 1997), the influence of environmentally ubiquitous humic acids on such processes appears as an interesting issue.

Experimental

Reagents and materials

The phenol (purity >99%), humic acid sodium salt, $\text{Fe}(\text{ClO}_4)_2$ (98%) and $\text{Fe}(\text{ClO}_4)_3$ (>99%) were from Aldrich, HClO_4 (70%) and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (>99%) from Merck, CH_3CN at supergradient grade from Scharlau.

Procedures

The reaction was carried out in magnetically stirred vials in the dark. Samples were analysed by high performance liquid chromatography-ultraviolet (HPLC-UV). Conditions: Merck-Hitachi chromatograph, flow rate 1.0 mL min^{-1} , 30:70 mixture of CH_3CN : phosphate buffer (pH 2.8), injection volume $54 \mu\text{L}$, detection wavelength 210 nm. The phenol retention time was 3.75 min. Solutions were filtered with $0.45\text{-}\mu\text{m}$ cellulose acetate Millipore HA membranes. Absorption was measured with a Varian Cary 100 Scan UV-Vis spectrophotometer, total organic carbon was measured with a Shimadzu TOC 5000 Analyzer.

Kinetic simulations

Kinetics of the systems was studied with the chemical kinetics simulator package: CKS shareware version, <http://www.almaden.ibm.com/st/msim/ckspage.html>.

Results and discussion

Fenton degradation of phenol

We have first studied the Fenton degradation of phenol alone, without humic acids. The time trend in the presence of $\text{Fe}(\text{II}) + \text{H}_2\text{O}_2$ is reported in Fig. 1. Phenol transformation takes place in two steps; the first is very fast and lasts less than 1 min. In the second step, which continues until phenol disappearance after about 70 min, the transformation rate is slower.

It is possible to explain the reported results by consideration of the kinetics of the various reactions involved in the Fenton process, initiated by the reaction as speci-

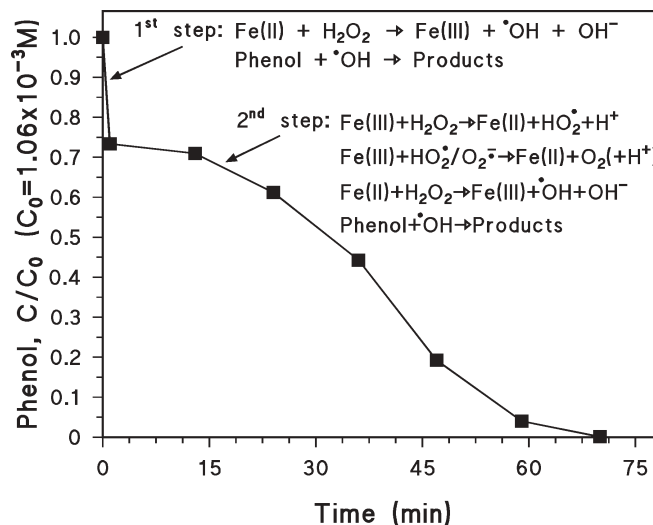
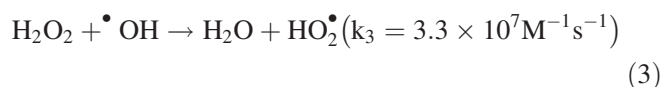
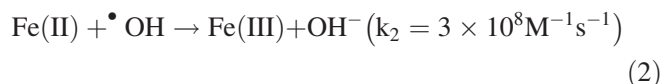


Fig. 1 Time trend of $1.06 \times 10^{-3} \text{ M}$ phenol with $3.0 \times 10^{-3} \text{ M}$ $\text{Fe}(\text{II})$ and 0.10 M H_2O_2 , pH 1 by HClO_4 . Phenol degradation occurs in two steps, the former lasting less than 1 min. Phenol transformation in the second step is much slower

fied by Eq. (1) between $\text{Fe}(\text{II})$ and H_2O_2 . The measured rate constant was $63 \text{ M}^{-1} \text{ s}^{-1}$ when following $\text{Fe}(\text{II})$ disappearance (De Laat and Gallard 1999). Hydroxyl generation in the reaction evidenced in Eq. (1) causes other processes:



The initial disappearance of $\text{Fe}(\text{II})$ and H_2O_2 can be modelled by the reactions demonstrated by Eqs. (1), (2), (3). In the presence of phenol, its reaction with $\cdot\text{OH}$ should also be considered at rate constant $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Boule et al. 1999). In the conditions adopted in Fig. 1, using an excess of H_2O_2 , $[\text{Fe}(\text{II})]$ would pass from 3.0×10^{-3} to $1.5 \times 10^{-5} \text{ M}$ in 1 min according to Chemical Kinetics Simulator runs. Figure 1 shows that phenol degradation initially proceeds very quickly, but the fast step lasts less than 1 min. Coherently with the simulation results, the fast step is driven by Eq. (1) reaction.

It is interesting to observe that our kinetic simulation foresees complete phenol disappearance within half a minute. The fact that the disappearance of the substrate seems to be slower or stoichiometrically defective when compared with the reaction between $\text{Fe}(\text{II})$ and H_2O_2 has already been observed by De Laat and Gallard (1999). Such results might constitute evidence in favour of Eq. (1) reaction being more complex than generally assumed, perhaps coherently with the hypotheses questioning an exclusive role of $\cdot\text{OH}$ in the Fenton reaction (Bossmann et al. 1998).

Because of the catalytic nature of the Fenton process after the first step, phenol degradation does, however, not

stop with Fe(II) consumption: $\text{Fe(III)} \rightarrow \text{Fe(II)} \rightarrow \text{Fe(III)}$ + $\cdot\text{OH}$. Fe(III) can in fact be reduced back to Fe(II) by H_2O_2 at a rate constant below $3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, by $\text{HO}_2\cdot$ ($\text{pK}_a=4.8$) at a rate constant of $1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, and by $\text{O}_2^{\cdot-}$ at a rate constant of $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (De Laat and Gallard 1999). Chemical kinetics simulator runs indicate that Fe(III) reduction by $\text{O}_2^{\cdot-}$ very soon becomes the prevailing process even at pH 1. $\text{O}_2^{\cdot-}$, the conjugate base of $\text{HO}_2\cdot$, is, however, not present from the beginning and has to accumulate upon reactions between Fe(III) and H_2O_2 and between H_2O_2 and $\cdot\text{OH}$.

Fe(III) reduction is operational in the second step of phenol degradation, which is slower than the first step and does not show a pseudo-first order kinetics. The pseudo-first order kinetics is absent also if one starts from phenol, Fe(III) and H_2O_2 ; only in this case one does not see the first step of the process. The fact that phenol degradation by Fe(III) and H_2O_2 does not follow a pseudo-first order kinetics is most likely due to the intermediates, which can both consume $\cdot\text{OH}$ and reduce Fe(III) to Fe(II). The first effect slows down the reaction, the second accelerates it. It has been shown that hydroquinone and other aromatics can enhance the Fenton process by reducing Fe(III) to Fe(II) (Chen et al. 2002). Phenol degradation intermediates, e.g. catechol and hydroquinone, are likely to reduce Fe(III) to Fe(II) more quickly than $\text{H}_2\text{O}_2/\text{HO}_2\cdot/\text{O}_2^{\cdot-}$.

The very fast first step of the reaction is difficult to follow by high performance liquid chromatography (HPLC), thus we have studied the second step. We have verified the equivalence of the two following procedures when operating in excess of hydrogen peroxide: (1) mix Fe(II) and H_2O_2 , wait a suitable time for Fe(II) to be consumed (e.g. 3 min), add phenol; (2) mix Fe(III), H_2O_2 and phenol. We are thus confident that procedure (2) placed us in a condition equivalent to the second step of the Fenton reaction, and isolated the effect of humic acids at this step. The second step is very representative of actual applications of the Fenton process because an excess of hydrogen peroxide is usually adopted and catalytic recycling of Fe extensively exploited.

Effect of humic acids

We then studied the effect of various concentration values of humic acids on the kinetics of the Fenton degradation of phenol. We focused on the second step, starting from Fe(III) and H_2O_2 . Figure 2 shows the time evolution of $2.65 \times 10^{-5} \text{ M}$ phenol in the presence of $1.0 \times 10^{-3} \text{ M}$ Fe(III) and $5.0 \times 10^{-3} \text{ M}$ H_2O_2 , at pH 2 by HClO_4 , with different amounts of humic acids. The transformation rate of phenol is higher in the presence of humic acids and increases with increasing humic acid concentration. This results in higher phenol concentration decrease at the beginning of the reaction and in shorter time required for complete phenol disappearance.

Phenol degradation in the absence of humic acids is due to Fe(III) reduction followed by the reaction evidenced by (1) yielding $\cdot\text{OH}$. The conditions adopted in

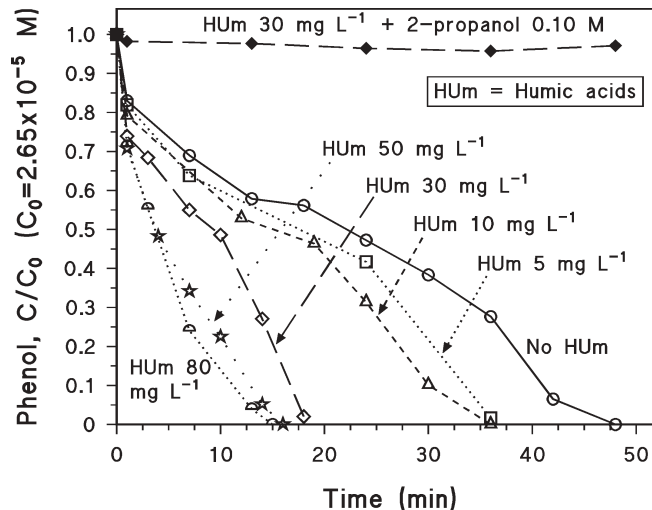


Fig. 2 Time trend of $2.65 \times 10^{-5} \text{ M}$ phenol with $1.0 \times 10^{-3} \text{ M}$ Fe(III), $5.0 \times 10^{-3} \text{ M}$ H_2O_2 , and different amounts of humic acids (HUm); pH 2 by HClO_4 . Humic acids increase phenol degradation rate

Fig. 2 are different from those shown in Fig. 1, but also in this case, phenol time evolution departs from a pseudo-first order kinetics. Figure 2 clearly shows that the addition of humic acids to the system increases phenol degradation rate.

Since humic acids form a precipitate in the presence of Fe(III) under the adopted conditions, at an induction time of 5–10 min, we have ensured that phenol time evolution was not biased in its possible partitioning on the precipitate. We have thus added 2-propanol to the system. The alcohol would scavenge $\cdot\text{OH}$, thus inhibiting phenol degradation, but would neither prevent precipitate formation, nor phenol partitioning on it. The time evolution of phenol in the presence of the Fenton reagent plus 30 mg L^{-1} humic acid and 0.10 M 2-propanol is reported in Fig. 2, indicating that phenol concentration in this case practically does not vary at all. As a consequence, phenol does not partition on the precipitate to a relevant extent and the time trend in the absence of 2-propanol is actually due to degradation.

Precipitate formation is due to the interaction between humic acids and Fe(III) and not to the fact of the reaction environment being acidic. Humic acids are insoluble at very low pH (De Laat and Gallard 1999), but the solubility at pH 2 is certainly higher than 80 mg L^{-1} , the highest concentration value we adopted. This is demonstrated by the absence of a visible precipitate and by the double absorbance at any wavelength of a 80 mg L^{-1} solution when compared with a 40 mg L^{-1} one. We have also verified that the humic acids sample that we used did not contain traces of Fe(II)/Fe(III), which in principle could explain the effect of humic acids on phenol transformation. Humic acids absorb radiation in the visible range: for the absorption spectrum of our sample see Fig. 1 in Vione et al. (2002). However, the spectral interference given by a 30 mg L^{-1} solution on the 510 nm spectrophotometric determination of Fe(II) as complex

with o-phenanthroline and on the 530 nm determination of Fe(III) as complex with thiocyanate is very limited. Furthermore, since the analytical blanks for the determination of both Fe(II) and Fe(III) showed negligible absorbance, the light extinction by humic acids could be taken into account. It is thus possible to conclude that our 30 mg L⁻¹ humic acids sample does not contain iron traces above 5.0×10⁻⁷ M.

Excluding the possible biases, the results we obtained and reported in Fig. 2 indicate that humic acids favour phenol degradation by Fe(III) and H₂O₂. The enhancement of phenol degradation rate by humic acids is even more marked in that humic acids can scavenge ·OH. The rate constant for the reaction of humic acids with hydroxyl is 1.9×10⁴ (mg of C L⁻¹)⁻¹ s⁻¹ (Goldstone et al. 2002). Total organic carbon data showed that our humic acids sample contains 42% C. The rate constant for phenol and ·OH is 1.4×10¹⁰ M⁻¹ s⁻¹ (Boule et al. 1999). Accordingly, the humic acid concentration giving an ·OH scavenging rate equal to the one of 2.65×10⁻⁵ M phenol is 20 mg of C L⁻¹, corresponding to 46 mg L⁻¹ humic acid. This means that humic acids would be the main ·OH scavengers in solution at the highest concentration values we adopted, but can somewhat interfere with the reaction between phenol and ·OH also in more dilute solutions. This consideration will further enforce the relevance of the finding concerning the enhancement of phenol degradation in the presence of humic acids.

The increase of phenol transformation rate in the presence of humic acids is most likely due to an acceleration of the reduction of Fe(III) to Fe(II); this process is rate-determining in the second step of the Fenton reaction (De Laat and Gallard 1999). It might thus be hypothesised that Fe(III) reduction is faster in the presence of humic acids. This hypothesis seems reasonable since, for instance, fulvic acids have been shown to reduce Fe(III) to Fe(II) in the dark (Voelker et al. 1997; Voelker and Sulzberger 1996). Interestingly, humic acids might positively influence Fenton degradation processes in a similar way as already demonstrated for hydroquinone and other aromatic compounds (Chen et al. 2002). We have however determined the formation rate of Fe(II) in the presence of 1.0×10⁻³ M Fe(III) and 30 mg L⁻¹ humic acids at pH 2. Fe(II) was below detection limit even after some days of reaction time. The results allow us to exclude that reduction of Fe(III) to Fe(II) upon direct reaction with humic acids can account for the humic acid effect on phenol degradation. A likely alternative is that Fe(III)-humate complexes undergo reduction to Fe(II) in the presence of H₂O₂/HO₂·/O₂^{·-} at a higher rate than Fe(III) aquocomplexes. This hypothesis implies that H₂O₂/HO₂·/O₂^{·-} are necessary as reducing agents and is supported by the precipitate formation in the presence of Fe(III) and humic acids, indicating that complex formation is possible. Moreover, Fe(II)-fulvate complexes have been shown to react with H₂O₂ faster than Fe(II) aquocomplexes (Voelker and Sulzberger 1996), and a similar effect for Fe(III)-humate complexes seems not unreasonable.

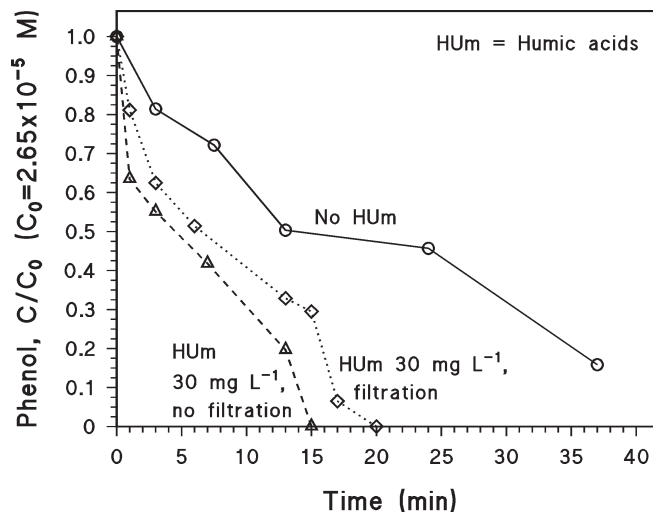


Fig. 3 Degradation of 2.65×10⁻⁵ M phenol with 1.0×10⁻³ M Fe(III), 5.0×10⁻³ M H₂O₂, and 30 mg L⁻¹ humic acids (HUM). pH 2 by HClO₄. In one run denoted by the empty diamond, the precipitate formed from Fe(III) and humic acids was filtered away before addition of phenol. Filtration has a detectable but secondary effect on the transformation rate of phenol

We have also investigated the role of the precipitate formed in the presence of Fe(III) and humic acids on the kinetics of phenol degradation. The whole experimental setup is reported below. The symbols correspond to the ones of Fig. 3:

1. O: Fe(III)+H₂O₂, wait 10 min, add phenol
2. Δ: Fe(III)+H₂O₂ + humic acid, wait 10 min, add phenol
3. ◇: Fe(III)+H₂O₂ + humic acid, wait 10 min including filtration time, add phenol

Figure 3 reports the time evolution of phenol in the absence and in the presence of humic acids. In one of the runs, the precipitate formed by Fe(III) and humic acids was removed by filtration after 10 min; this procedure slightly decreases the transformation rate of phenol when compared with the unfiltered sample. Figure 3 does, however, indicate that the major effect on phenol degradation is linked with the presence or absence of humic acids in the system. Filtration only plays a secondary role on phenol degradation. It can thus be inferred that the filter-removable Fe(III)-humic acid precipitate does not play a major role in Fe(III) reduction. Furthermore, the filtered solution still contains humic acids as indicated by its colour and spectral properties. Evidently, in the heterogeneous mixture present in the humic acid sample, there are components forming particles larger than 0.45 μm in the presence of Fe(III), and other ones forming either smaller particles or soluble complexes. Considering that Fe(III)-humate complexes are likely to be involved in enhanced Fe(III) reduction, it is possible that the majority of these active complexes are not incorporated in particles larger than 0.45 μm.

The data shown here on the enhancement of Fenton degradation by humic acids, together with an enhancement effect reported for a variety of aromatic compounds (Chen et al. 2002), indicate that the Fenton reaction might be affected by the presence of water-dissolved natural organic compounds a lot less negatively than other remediation techniques.

Conclusion

Humic acids favour the degradation of phenol in the presence of $\text{Fe(III)} + \text{H}_2\text{O}_2$. Their effect is likely due to enhanced reduction of Fe(III) -humate complexes to Fe(II) by $\text{H}_2\text{O}_2/\text{HO}_2^\cdot/\text{O}_2^{\cdot-}$, when compared with Fe(III) aquo-complexes. Fe(II) thus formed reacts with H_2O_2 to yield $^\cdot\text{OH}$, which is responsible for phenol degradation. This effect of humic acids is relevant to the practical applications of the Fenton reaction, where the catalytic cycles of Fe(III) reduction are extensively exploited. The results shown in this paper indicate that the Fenton technique might be very conveniently applied to treat water with high humic acid concentration, and in particular contaminated soil extracts. Furthermore, these data also show that natural aquifers rich in humic acids have an increased self-depuration capacity as far as Fenton processes are concerned.

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