Activation of Persulfate by Irradiated Magnetite: Implications for the Degradation of Phenol under Heterogeneous Photo-Fenton-Like Conditions

(Article begins on next page)

23 November 2024

UNIVERSITÀ DEGLI STUDI DI TORINO

Activation of persulfate by irradiated magnetite: Implications for the degradation of phenol under heterogeneous photo Fenton-like conditions

Paola Avetta,[a] Alessia Pensato,[a] Marco Minella,[a] Mery Malandrino,[a] Valter Maurino,[a] Claudio Minero,[a] Khalil Hanna,[b,]* Davide Vione [a,]*

[a] *Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 5, 10125 Torino, Italy.*
[b] *Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France.*

* Address correspondence to either author. Tel: +39-011-6705296; Fax +39-011-6705242 (D. Vione); Tel. +33-(0)2-23238027; Fax +33-(0)2-23238120 (K. Hanna). E-mail: *davide.vione@unito.it* (D. Vione), *khalil.hanna@ensc-rennes.fr* (K. Hanna).

Abstract

We show that phenol can be effectively degraded by magnetite in the presence of persulfate ($S_2O_8^{2-}$) under UVA irradiation. The process involves the radical $SO_4^{-\bullet}$, formed from $S_2O_8^{2-}$ in the presence of Fe^{II}. Although magnetite naturally contains Fe^{II}, the air-exposed oxide surface is fully oxidized to Fe^{III} and irradiation is required to produce Fe^{II}. The magnetite + $S_2O_8^{2-}$ system was superior to the corresponding magnetite + H_2O_2 one in the presence of radical scavengers and in a natural water matrix, but it induced phenol mineralization in ultra-pure water to a lesser extent. The leaching of Fe from the oxide surface was very limited, and much below the wastewater discharge limits. The reasonable performance of the magnetite/persulfate system in a natural water matrix and the low levels of dissolved Fe are potentially important for the removal of organic contaminants in wastewater.
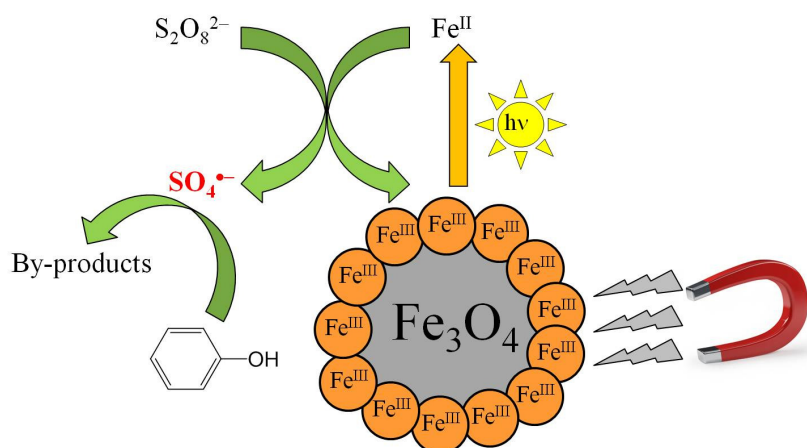
Introduction

The sulfate radical ($SO_4^{-\bullet}$) is a strong one-electron oxidant.[1] Its properties, including the reactivity with organic compounds, have been determined in early studies where $SO_4^{-\bullet}$ was generated by radiolysis of persulfate solutions.[2,3] The activation of persulfate ($S_2O_8^{2-}/SO_4^{2-}$, $E° = 2.01$ V $vs.$ NHE) to generate $SO_4^{-\bullet}$ ($SO_4^{-\bullet}/SO_4^{2-}$, $E° = 2.6$ V $vs.$ NHE) was recently proposed to remove different kinds of organic pollutants in contaminated waters and soils.[4-6] Persulfate activation to $SO_4^{-\bullet}$ can be initiated under photochemical, thermal (also with metal catalysts) or chemical conditions, and $SO_4^{-\bullet}$ can rapidly react with several organic compounds with second-order rate constants in the range of 10^7-10^{10} M^{-1} s^{-1}.[7] Iron (often as dissolved Fe^{2+}) is a commonly used transition metal for the chemical activation of persulfate:[8-10]

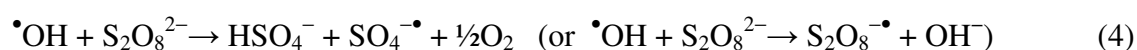$$Fe^{II} + S_2O_8^{2-} \rightarrow Fe^{III} + SO_4^{2-} + SO_4^{-\bullet} \tag{1}$$

The $^{\bullet}OH$ radical can also be produced in the presence of $SO_4^{-\bullet}$. Reaction (2) takes place under basic conditions:[9]

$$SO_4^{-\bullet} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \tag{2}$$

and reaction (3) at all pH values:

$$SO_4^{-\bullet} + H_2O \rightarrow {}^{\bullet}OH + HSO_4^- \tag{3}$$

Liang et al. [4] suggested that $SO_4^{-\bullet}$ predominates under acidic conditions and $^{\bullet}OH$ under alkaline ones. Both $^{\bullet}OH$ and $SO_4^{-\bullet}$ could attack target contaminants, but they can also react with the persulfate anion as follows:[7]

$$^{\bullet}OH + S_2O_8^{2-} \rightarrow HSO_4^- + SO_4^{-\bullet} + \tfrac{1}{2}O_2 \quad (\text{or } {}^{\bullet}OH + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + OH^-) \tag{4}$$

$$SO_4^{-\bullet} + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + SO_4^{2-} \tag{5}$$

Other competitive or scavenging reactions may occur (although reaction (7) would be minor in the presence of organic compounds):[7,9,11]

$$Fe^{II} + SO_4^{-\bullet} \rightarrow Fe^{III} + SO_4^{2-} \tag{6}$$

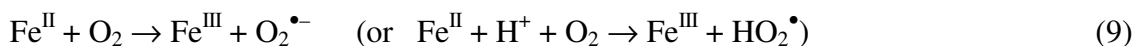$$2\,SO_4^{-\bullet} \rightarrow S_2O_8^{2-} \tag{7}$$

Because of similarities between the activation of persulfate by Fe^{II} and the Fenton reaction, the persulfate process is usually named Fenton-like.

The main drawback of dissolved Fe^{II} (Fe^{2+}) is the rapid oxidation and precipitation as Fe^{III}, which inactivates ferrous iron. Chelating agents have been used to maintain Fe^{III} in solution, where it can be more easily recycled to Fe^{II}.[8,12] In alternative, the UV irradiation of Fe^{III} species is an interesting Fe^{II} source.[13,14] Another possibility is the use of minerals such as

ferrihydrite, goethite, manganese oxide and clay (including modified clays),[15,16] which can activate persulfate and induce the degradation of *e.g.* trichloroethylene or diesel compounds.[5,17] Magnetite (Fe_3O_4) is a good agent to activate persulfate in the remediation of PAH-contaminated soil.[18] Fe_3O_4 is one of the most stable mixed-valence oxides (Fe^{II}-Fe^{III}) at ambient temperature, and it is the most abundant in natural settings. Moreover, it can be synthesized in the laboratory by various biotic and abiotic pathways. Depending on the source or the synthesis method, magnetites with different composition, crystal habits, morphologies and surface properties can be produced.[19]

  In addition to the magnetic properties that facilitate phase separation, the natural presence of Fe^{II} in magnetite has understandably attracted attention in the field of heterogeneous Fenton and Fenton-like reactions.[20,21] Moreover, we have recently found that the Fenton reactivity of magnetite can be considerably enhanced under irradiation.[22] The traditional photo-Fenton process is exemplified in reactions (8-13), according to the proposed Haber-Weiss mechanism, and it is particularly useful with sunlight as radiation source.[23] Note that *L* is an intentionally added or naturally occurring organic ligand (*e.g.* citrate, oxalate or ligand moieties of dissolved organic matter). The $^{\bullet}OH$ yield of reaction (13) is not quantitative, and additional oxidants (*e.g.* ferryl, FeO^{2+}) could also be formed in the process:[24,25]

$$Fe^{III}OH^{2+} + h\nu \rightarrow Fe^{II} + {}^{\bullet}OH \tag{8}$$

$$Fe^{II} + O_2 \rightarrow Fe^{III} + O_2^{\bullet-} \quad (or \quad Fe^{II} + H^+ + O_2 \rightarrow Fe^{III} + HO_2^{\bullet}) \tag{9}$$

$$HO_2^{\bullet} + O_2^{\bullet-} + H^+ \rightarrow H_2O_2 + O_2 \tag{10}$$

$$Fe^{III} + O_2^{\bullet-} \rightarrow Fe^{II} + O_2 \tag{11}$$

$$Fe^{III}\text{-}L + h\nu \rightarrow Fe^{II} + L^{+\bullet} \tag{12}$$

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III} + {}^{\bullet}OH + OH^- \tag{13}$$

The use of magnetite to activate persulfate under irradiation has never been tested to date. Therefore, the goal of the present work is, first of all, to provide the very first evidence to our knowledge of the feasibility of the process for the degradation of organic compounds in both synthetic and natural water matrices. Considering that magnetite exists as micrometric and nanometric particles in many natural and engineered systems, four kinds of synthetic magnetites with different particle size and stoichiometry were tested in dark and irradiation experiments. Insights are given into the possible reactive species involved in the degradation pathways, and the systems magnetite + H_2O_2 + UV and magnetite + $S_2O_8^{2-}$ + UV are compared for the degradation and mineralization of phenol.

Experimental section

Reagents and materials

Phenol (purity grade 99%), 1,10-phenanthroline (99%), 2-propanol (99.9%), potassium hydrogen phthalate (99%), KI (98%), $NaHCO_3$ (99%), NaH_2PO_4 (99%), Na_2HPO_4 (98%), 4-aminoantipyrine (98%), K_2CO_3 (99%), H_3PO_4 (85%), $HClO_4$ (70%), magnetite (97%), methanol (gradient grade) and horseradish peroxidase (type VI) were purchased from Sigma-Aldrich, $Na_2S_2O_8$ (99%) from Fluka, magnetite (98%) from Prolabo, H_2O_2 (35%) from VWR International, argon (research grade) and zero-grade air from Sapio (Monza, Italy). All reagents were used as received, without further purification. The aqueous solutions were prepared by using Milli-Q water (TOC < 2 ppb, resistivity ≥18.2 mΩ cm).

Concerning the used magnetite specimens, two (S1 and S2) were synthesized by Fe^{II}-induced mineralogical transformation of 2-line ferrihydrite and lepidocrocite (γ-FeOOH), respectively, as explained in detail in previous works.[22,26] Magnetite S3 was purchased from Prolabo and S4 from Aldrich. Sample characterization is explained in the Supporting Information (hereafter SI). Table 1 reports particle size, surface area, the pH values of the point of zero charge (pH_{PZC}, estimated from potentiometric titration), and the Fe^{II}/Fe^{III} ratios of the oxides. The latter were determined by chemical analysis after acid dissolution, as suggested by Gorski et al. [27] who reported an excellent agreement with Mössbauer spectroscopy.

The ratio between ferrous and ferric ions ($x = Fe^{II}/Fe^{III}$) was lower than 0.5, thus all the investigated samples may be considered as non-stoichiometric or partially oxidized magnetite.[27,28] The most oxidized samples (lowest x values) were S1 and S4.[26,27] S4 is a commercial sample, but S1 could still contain precursor ferrihydrite as residual from the synthesis method. This is supported by TEM images (Figure S1-SI) and by the high PZC value of S1 (close to that of ferrihydrite, *i.e.* ~8.2,[19] Table 1). Abiotic synthesis methods (as for samples S1 and S2) generally fail to generate stoichiometric magnetite,[27,28] probably because the washing step(s) easily cause Fe^{2+} dissolution/oxidation.[27,29] Characterization of S1-S4 by X-ray powder diffraction (XRD) only gave the main magnetite diffraction peaks, while other crystallographic phases were lower than the XRD limit of detection (around 5%).

The PZC of S2-S4 (Table 1) is close to literature reports for magnetite.[19] An expected inverse proportionality was observed between BET surface area and particle size. Significant aggregation of magnetite particles in aqueous suspension is suggested by the comparison of the particle size data estimated from TEM images (Table 1) with the hydrodynamic radii from Dynamic Light Scattering (DLS, Figure S1-SI). Further details about the characterization methods, including XRD, TEM-EDAX (Transmission Electron Microscopy-Energy Dispersive X-ray spectrometry), multipoint N_2–BET and DLS analyses are given in the SI.

Irradiation experiments

Magnetite stock suspensions at 1.0 g L^{-1} loading were prepared by ultrasonication (Branson 2200 ultrasonic bath, 40 kHz). The suspensions for irradiation (50 mL total volume in a beaker) were prepared by diluting stock suspensions to 0.2 g L^{-1}. Phenol, H_2O_2 and persulfate were added from separate stock solutions. The natural pH value of the system was ~5, measured (and periodically monitored as irradiation progressed) with a combined glass electrode connected to a Metrohm 713 pH meter. Irradiation took place under a 20 W Philips TL 09N UVA lamp, with emission maximum at 365 nm. The lamp irradiance on top of the suspensions was 18 W m^{-2} in the 295-400 nm range, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. The suspension temperature was ~30°C. A picture showing the experimental set-up is provided in the supplementary material of previous work.[22] Irradiation experiments were carried out in duplicate, the results averaged and the error bars reported on the relevant plots.

To monitor the time evolution of phenol, aliquots of ~1.5 mL were withdrawn from the irradiated suspension at selected time intervals and immediately filtered on Millipore HV syringe filters (Teflon, 0.45 µm pore diameter). A precisely measured volume (0.7 mL) of the filtered solution was immediately added to an HPLC vial, containing 0.7 mL methanol to quench the reaction. Analysis within the shortest possible time was carried out by high-performance liquid chromatography coupled to diode array detection (HPLC-DAD). In some experiments, larger aliquots (5 mL) were withdrawn to monitor persulfate and H_2O_2 (UV-Vis spectrophotometry), sulfate and carboxylic acids (ion chromatography), as well as total dissolved Fe (inductively coupled plasma). Further analytical details are provided as SI.

The analysis of total organic carbon (TOC) was carried out on filtered-only sample aliquots, without methanol addition, by using a Shimadzu TOC-V$_{CSH}$ Total Organic Carbon Analyzer, equipped with an ASI-V autosampler and fed with zero-grade air. The TOC was determined as total carbon minus inorganic carbon.

Natural water was sampled in summer 2013 from the surface of the eutrophic Lake Candia (near Torino, NW Italy) and vacuum filtered upon arrival to the laboratory (cellulose acetate filters, 0.45 µm, Sartorius). Sampled water had the following features: 7±1 mg L^{-1} Ca, 18±2 mg L^{-1} Mg, 15±1 µg L^{-1} nitrate, 6.9±1.0 mg C L^{-1} TOC, 12±1 mg C L^{-1} inorganic carbon, pH 8.3.

Results and Discussion

Preliminary runs were carried out to look for the main factors involved in phenol degradation and to check for the optimal experimental conditions. The degradation of phenol with magnetite usually required the contemporary presence of radiation and an oxidant (H_2O_2 or persulfate). The optimal magnetite loading was 0.2 g L^{-1}, most likely because higher loadings would cause excessive scattering of radiation by the suspension.[22]

The need to apply radiation could be avoided at elevated persulfate concentration, and effective transformation of 0.1 mM phenol took place with 50 mM $S_2O_8^{2-}$ in the dark. In this case the suspension pH dropped from ~5 to ~3 in less than 2 h, followed by very limited further changes up to at least 24 h. Phenol degradation in the dark with 50 mM $S_2O_8^{2-}$ also took place without magnetite, thereby suggesting that persulfate can directly react with phenol. The reaction would cause an initial pH decrease, as a consequence of the oxidation of the organic substrate with production of sulfuric acid (see for instance reaction (14), where HPhOH represents phenol):[30]

$$HPhOH + S_2O_8^{2-} + H_2O \rightarrow HOPhOH + 2\ SO_4^{2-} + 2\ H^+ \tag{14}$$
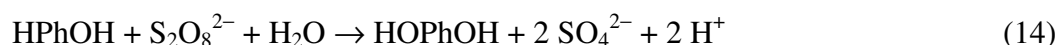
Due to contact with air, the surface layer of magnetite is fully oxidized to Fe^{III}.[27] The initial acidification would cause dissolution of surface Fe^{III}, letting sub-surface Fe^{II} in contact with the aqueous phase. Persulfate activation and further acidification would proceed as follows:[30]

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-} \tag{15}$$
$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \tag{16}$$

The formation of poorly soluble Fe^{III} species would limit the concentration of dissolved Fe, which was around 0.1 mg L^{-1}. Moreover, acidification due to reactions (14-16) would induce an additional pathway of persulfate activation (reactions (17,18), with no net pH impact):[30,31]

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{17}$$
$$HS_2O_8^- \rightarrow 2\ SO_4^{-\bullet} + H^+ \tag{18}$$

Differently from 50 mM persulfate, little to no degradation of phenol was observed with 0.5 mM $S_2O_8^{2-}$ alone (without magnetite), either in the dark or under irradiation. In this case, both magnetite and UVA radiation were required for phenol degradation. Further experiments with the irradiated systems suggested that no transformation was operational with phenol + UVA or with phenol + magnetite + UVA. The blank runs also showed negligible adsorption of phenol on magnetite.

Phenol degradation by magnetite + $S_2O_8{}^{2-}$ + UVA: effect of the Fe_3O_4 specimen

Figure 1 shows the time trend of 0.1 mM phenol in the presence of 0.5 mM $S_2O_8{}^{2-}$ under UVA irradiation, with no magnetite and in the presence of each of the studied magnetite specimens (S1 to S4, at a loading of 0.2 g L^{-1} each). Compared to the experiment without magnetite, all the S1-S4 samples enhanced phenol transformation. The enhancement was highest for S2 and S3.

The elevated photoactivity of S2 and S3, compared to S1 or S4, cannot be accounted for by differences in particle size or surface area (see Table 1). However, S2 and S3 are the studied magnetite specimens with the highest structural content of Fe^{II} (Table 1). The link between Fe^{II} content and photo-Fenton or photo-Fenton-like reactivity is only apparently straightforward (Fe^{II} is the most reactive Fe species towards peroxides),[32] because the studied magnetites were unreactive in the dark with 0.5 mM $S_2O_8{}^{2-}$. The insignificant dark reactivity is in clear contrast with a simple hypothesis concerning the availability of Fe^{II} at the magnetite surface, which would be higher for S2 and S3 compared to S1 and S4. The need to irradiate the system suggests that Fe^{III} is the primary actor of magnetite photoreactivity, because Fe^{II} species are often photochemically inactive.[14] Radiation absorption by Fe^{III} compounds (including the hydroxocomplexes) is linked to a ligand-to-metal charge transfer and the photolysis induces Fe^{III} reduction to Fe^{II}, together with ligand oxidation (see reaction 8).[33,34]

To account for the observed phenomena one should consider that, although bulk magnetite contains Fe^{II}, its air-exposed surface is substantially or totally oxidized to Fe^{III}. Indeed, Fe^{II} in the outer regions reacts with atmospheric O_2 and forms a thin layer of epitaxial maghemite.[27,35] The oxidation process occurs to a depth of approximately 3 nm and depends on particle size and lattice order.[36] Surface oxidation was confirmed by XPS analysis of the investigated samples (see Figure S2-SI), and it is corroborated by the relatively low values of Fe^{II}/Fe^{III} (Table 1). Fe^{III} photoreduction is thus required to produce Fe^{II} that activates persulfate. Note that magnetite stoichiometry (Fe^{II}/Fe^{III}) may influence its overall reactivity, including sorption capacity and reduction potential.[29]

In the presence of the photoactive magnetites S2 and S3, the suspension pH dropped from ~5 to ~4 upon irradiation. Considering that the direct reaction (14) between phenol and persulfate can be excluded (no degradation of 0.1 mM phenol was observed with 0.5 mM $S_2O_8{}^{2-}$), the pH drop would be accounted for by reactions (15,16). In these systems, dissolved Fe was detectable but quite low (< 0.1 mg L^{-1}). Fe leaching is a potential problem because of the limits for wastewater discharge, but Fe levels below 0.1 mg L^{-1} are safe from this point of view.[15] The detected concentration of total Fe also places an upper limit for the possible scavenging of $SO_4{}^{-\bullet}$ by dissolved Fe^{2+}, based on the reported reaction rate constants:[7]

compared to phenol, Fe^{2+} would scavenge <1% $SO_4^{-\bullet}$ at the beginning of the reaction and the process would become important only after almost complete phenol removal.

Effect of persulfate concentration

The effect of variable persulfate concentration on the transformation of phenol was studied in the presence of the photoactive samples S2 and S3. A $[S_2O_8^{2-}]$ increase from 0.5 to 5 and then to 50 mM understandably accelerated the degradation of phenol. With S2, the respective phenol half-life times decreased from about 10 to ~3 and ~1 hour. The corresponding data for S3 were ~10, ~2.5 and <1 h.

At 0.5 mM $S_2O_8^{2-}$ the degradation of phenol was much faster with S2 or S3 compared to persulfate alone, without magnetite (see Figure 1), but the magnetite effect became considerably less important with increasing $S_2O_8^{2-}$. Figure 2 reports the time trend of 0.1 mM phenol in the presence of 50 mM $S_2O_8^{2-}$, with and without magnetite (S2) and with and without irradiation. First of all, when using 50 mM $S_2O_8^{2-}$ and despite the acceleration observed with S2, considerable phenol transformation was already achieved with irradiated persulfate alone. $S_2O_8^{2-}$ undergoes photolysis upon UV absorption, yielding $SO_4^{-\bullet}$ [37] that is able to oxidize phenol.[7] The importance of persulfate photolysis would increase with increasing persulfate concentration, while competition for irradiance between magnetite and persulfate might account for the limited S2 effect. The magnetite specimen S3 was slightly more active compared to S2 (data not shown), but the overall behavior was quite similar.

Figure 2 shows that some degradation of phenol with 50 mM $S_2O_8^{2-}$ already occurred in the dark, also without magnetite, possibly due to reactions (14,17,18). Overall, the experiments with variable persulfate concentration suggest that the addition of magnetite is very useful at low persulfate (0.5 mM in the present case), and much less effective at elevated oxidant levels. Irradiated magnetite allows a persulfate economy that has potential advantages from an applicative point of view, including the lower initial cost of the oxidant (which would not be offset by the cost of radiation if sunlight is used) and the lesser need to eliminate the oxidant excess after treatment.

Effect of the addition of 2-propanol

The degradation of phenol by activated persulfate could occur upon reaction with $SO_4^{-\bullet}$ and/or $^\bullet OH$. Insight into phenol transformation pathways with magnetite + persulfate + UVA could be obtained by studying the effect of 2-propanol. The alcohol reacts with both $^\bullet OH$ and $SO_4^{-\bullet}$,[38] but the second-order reaction rate constant with $^\bullet OH$ ($1.9 \cdot 10^9$ M^{-1} s^{-1}) is around 45-50 times higher than that with $SO_4^{-\bullet}$ ($4 \cdot 10^7$ M^{-1} s^{-1}).[7,39] In contrast, the reaction rate constant

between phenol and $^\bullet OH$ ($6.6 \cdot 10^9$ M^{-1} s^{-1}) is only 3 times higher than the phenol rate constant with SO$_4^{-\bullet}$ ($2.2 \cdot 10^9$ M^{-1} s^{-1}).[39,40]

Persulfate was used at 0.5 mM initial concentration, where the magnetite effect on degradation was very significant. The second-order reaction rate constant between persulfate and SO$_4^{-\bullet}$ ($1.2 \cdot 10^6$ M^{-1} s^{-1})[7] ensures that 0.5 mM S$_2$O$_8^{2-}$ scavenges SO$_4^{-\bullet}$ to a negligible extent compared to 0.1 mM phenol. A similar issue happens with $^\bullet OH$, given the very low second-order reaction rate constant with persulfate ($<1 \cdot 10^6$ M^{-1} s^{-1}).[39] The following discussion focuses on S2, but fully comparable results were obtained with S3.

Figure 3a compares phenol phototransformation with S2 (0.2 g L^{-1} loading), with and without 2-propanol (2 mM initial concentration when applicable), in the presence of 0.5 mM S$_2$O$_8^{2-}$. The addition of 2-propanol induced limited inhibition of phenol transformation. As mentioned above, phenol and 2-propanol could react with both $^\bullet OH$ and SO$_4^{-\bullet}$, while the scavenging of radical species by S$_2$O$_8^{2-}$ would be negligible.[7,40] In the absence of 2-propanol, practically all the photogenerated $^\bullet OH$ and SO$_4^{-\bullet}$ would react with phenol. In the runs with the alcohol, 2 mM 2-propanol (in competition with 0.1 mM phenol) would scavenge ~85% of the photogenerated $^\bullet OH$ but only 25% of SO$_4^{-\bullet}$, while the rest would react with phenol. Therefore, 2 mM 2-propanol should strongly inhibit the transformation of 0.1 mM phenol if $^\bullet OH$ were the main reactive species, while the effect of the alcohol should be relatively small if the reaction with SO$_4^{-\bullet}$ were the prevailing process. The experimental data of Figure 3a support the hypothesis that phenol degradation would prevalently take place upon reaction with SO$_4^{-\bullet}$.

It is interesting to compare the persulfate results with those obtained using H$_2$O$_2$. Figure 3b shows the time trends of 0.1 mM phenol in the presence of S2 (0.2 g L^{-1} loading) and 0.5 mM H$_2$O$_2$, with and without 2 mM 2-propanol. The reaction rate constant between H$_2$O$_2$ and $^\bullet OH$ ($2.7 \cdot 10^7$ M^{-1} s^{-1})[39] ensures that $^\bullet OH$ scavenging by hydrogen peroxide would be ~50 times lower compared to phenol. Therefore, in the absence of 2-propanol, phenol would be the main $^\bullet OH$ scavenger in the irradiated system. In the presence of 2 mM 2-propanol, as mentioned above, 85% $^\bullet OH$ would react with the alcohol and only 15% with phenol. The experimental data support this assumption and they are, therefore, consistent with the involvement of $^\bullet OH$ in the degradation of phenol with S2 + H$_2$O$_2$ + UVA. However, it should be pointed out that the controversy concerning the role of $^\bullet OH$ $vs.$ super-oxidized iron species ($e.g.$ the ferryl ion, FeO^{2+}) in Fenton degradation is not totally solved.[41-43] While it could be reasonably assumed that ferryl might be more activated to electron-transfer processes than to H-abstraction,[25] too little is presently known about its reactivity with organic compounds to derive a definite conclusion.

Briefly, $^\bullet OH$ can be ruled out as an important reactive species for the degradation of phenol with S2 + S$_2$O$_8^{2-}$ + UVA (SO$_4^{-\bullet}$ would rather be involved). In contrast, the

experimental data for S2 + H_2O_2 + UVA are consistent with phenol degradation by $^\bullet$OH, although they are silent regarding a possible role of additional species (*e.g.* ferryl).

Trend of the total organic carbon

Substrate mineralization is a welcome target in degradation processes, because it avoids the potential problem of the formation of recalcitrant intermediates as potential secondary pollutants. In the case of phenol it is well known that transformation causes detoxification in the vast majority of cases,[44,45] but the problem of the intermediates could be very important with other substrates.[46,47] Therefore, the time trend of the total organic carbon (TOC) was monitored in the presence of the photoactive specimen S2 (S2 + $S_2O_8^{2-}$ + UVA, see Figure 4a). For comparison, the TOC trend was also monitored in the system S2 + H_2O_2 + UVA. Because phenol mineralization was considerably slower than degradation, in the relevant experiments the initial concentration values of persulfate and H_2O_2 were increased to 5 mM. The corresponding runs carried out in the dark (data not shown) yielded no TOC variation for S2 + $S_2O_8^{2-}$. In the case of S2 + H_2O_2 in the dark, the TOC was stable for the first 50 h and then it decreased by approximately 50% till 70 h.

Figure 4a suggests that some degree of mineralization under irradiation took place in both cases. The TOC decrease was initially comparable for $S_2O_8^{2-}$ and H_2O_2, but in the case of persulfate it practically stopped after 48 h. In contrast, complete mineralization was achieved with H_2O_2 after 70 h irradiation. In the case of H_2O_2, the pH of the irradiated suspension slightly decreased from ~5 to ~4.5 within 24 h, and it was then approximately stable as irradiation progressed. With persulfate, the pH dropped to ~3 within 24 h and tended towards 2 for longer irradiation times. It should be underlined that both the degradation and the mineralization of organic compounds by $S_2O_8^{2-}$/$SO_4^{-\bullet}$ are favored under acidic conditions,[30] thus the pH drop cannot account for the lack of phenol mineralization by S2 + $S_2O_8^{2-}$ + UVA after 48 h irradiation.

A possible explanation for the trend reported in Figure 4a could be a higher instability of $S_2O_8^{2-}$ compared to H_2O_2: if the reaction mixture runs out of persulfate at around 48h, it is reasonable that the mineralization process cannot continue. However, Figure 4b shows that persulfate was a bit more stable than H_2O_2, which rules out such a hypothesis. Figure 4c additionally shows that there was a practically quantitative conversion of $S_2O_8^{2-}$ into SO_4^{2-} (note that one persulfate ion can produce two sulfate ions).

An alternative explanation is that $SO_4^{-\bullet}$ has more variable reaction rate constants toward organic compounds compared to $^\bullet$OH (see Figure S3-SI and related discussion).[7,39] Therefore, the probability that phenol degradation produces a refractory intermediate would be higher with $SO_4^{-\bullet}$ than with $^\bullet$OH. In the persulfate experiments, trace levels of acetic acid and a buildup of formic acid were observed. Both compounds would be formed upon ring opening

and fragmentation,[48,49] and formic acid reached 0.15 mM levels at the longest irradiation time. Under such conditions, it would account for ~25% of the initial carbon and for almost 50% of the residual one. Interestingly, $^\bullet$OH is much more reactive than $SO_4^{-\bullet}$ towards formic acid.[7,39]

Performance of magnetite/$S_2O_8^{2-}$/UVA and magnetite/H_2O_2/UVA in a natural water matrix

The systems based on $S_2O_8^{2-}$/$SO_4^{-\bullet}$ may be more effective than their H_2O_2/$^\bullet$OH homologues in inducing degradation reactions in the presence of natural water components that scavenge $^\bullet$OH.[50,51] On the other hand, persulfate may be less performing than H_2O_2 in waters that are poor in *e.g.* dissolved organic matter (the main $^\bullet$OH scavenger in natural waters).[52,53]

To check for the above suggestions, the degradation of phenol was also studied in a natural water matrix from a eutrophic lake (Lago di Candia, province of Torino, Piedmont region, NW Italy). Water from this lake was chosen because it is relatively rich of organic matter and very poor (sub-µM levels) of nitrate, which is a photochemical $^\bullet$OH source and might potentially act as a confounding factor.[54,55] Moreover, the very low Fe levels in filtered lake water (~2 µg L^{-1}) suggest that naturally occurring Fe would not be able to trigger Fenton or Fenton-like processes to a significant extent. Phenol was added to lake water at an initial concentration of 10 µM, to ensure that it was not the main contributor to the total organic carbon (TOC) of the sample. Indeed, 10 µM phenol has TOC = 0.72 mgC L^{-1}, to be compared with TOC ~7 mgC L^{-1} accounted for by natural organic matter in lake water. The oxidants ($S_2O_8^{2-}$ or H_2O_2, where relevant) were used at equal concentration (0.5 mM).

Figure 5 shows that, when irradiation was carried out in the lake water matrix, phenol degradation was more effective in the presence of S2 + $S_2O_8^{2-}$ compared to S2 + H_2O_2. Both the persulfate- and the H_2O_2-based Fenton(-like) systems tend to show lesser performance at basic pH and in the presence of carbonate/bicarbonate buffers, which can scavenge reactive radicals.[30,41-43] Water from Lake Candia had pH 8.3 and about 1 mM of inorganic carbon, which would slow down the kinetics of phenol degradation with both H_2O_2 and $S_2O_8^{2-}$. Interestingly, chloride is expected to interfere with H_2O_2-based systems to a higher extent than with those containing persulfate.[56] The photo-Fenton system (H_2O_2-based) has two further disadvantages over the persulfate one: the first is that natural organic matter scavenges $^\bullet$OH to a higher extent than $SO_4^{-\bullet}$,[50,51] the second is that increasing pH decreases the yield of $^\bullet$OH (reaction (13)). Indeed, while at pH 2-3 the $^\bullet$OH yield is approximately 60%,[25] at higher pH the $^\bullet$OH production decreases and the reaction is shifted towards ferryl.[41-43] The latter is considerably less reactive than $^\bullet$OH,[25] and a significant decrease of the system reactivity is usually observed.[15]

Possible implications for water treatment

This paper shows, for the first time to our knowledge, that magnetite under UVA irradiation can activate persulfate to $SO_4^{-\bullet}$ and induce effective degradation of phenol, used as model pollutant. Magnetite irradiation was necessary to photoreduce Fe^{III} to Fe^{II} because, although the oxide contains structural Fe^{II}, its surface is oxidized by contact with atmospheric O_2.

The magnetite/persulfate/UVA system was less affected than the corresponding H_2O_2-based one by the presence of radical scavengers or a natural water matrix. This probably happened for two reasons: *(i)* $SO_4^{-\bullet}$ is less subject than $^\bullet OH$ and/or ferryl (possible reactive species in the H_2O_2-based Fenton systems) to the scavenging reactions by organic compounds and natural organic matter, and *(ii)* (only for natural water) the reactivity of the H_2O_2-Fenton system is decreased to a higher extent than the persulfate one in neutral to basic conditions, because of the decreased $^\bullet OH$ yield. However, despite a slightly higher stability of $S_2O_8^{2-}$ *vs.* H_2O_2 at long irradiation times, the persulfate system was inferior to the H_2O_2 one as far as phenol mineralization was concerned. Therefore, the selection of the most suitable process might depend on the water matrix to be treated.

Heterogeneous Fenton and Fenton-like systems can have the advantage of a limited amount of dissolved Fe, which may save the need to eliminate the Fe excess at the end of the treatment (*e.g.* by precipitation). In our systems the Fe level was much below 1 mg L^{-1}, *i.e.* the limit above which Fe elimination from wastewater would be necessary. Further advantages are the effectiveness under UVA light, which allows the use of cheap sunlight that would offset the relatively slow reaction kinetics, and the easy magnetic separation of magnetite nanoparticles at the end of the treatment. In the case of persulfate a disadvantage is represented by acidification as reaction progresses, which would require pH correction after treatment. In contrast, the use of buffers to maintain the pH at higher levels is well-known to inhibit the $S_2O_8^{2-}$-based Fenton-like processes.[30]

The reaction of oxidants with the magnetite surface could induce mineralogical transformation and/or a substantial change in the surface characteristics. While the photocorrosion of the oxide is of little importance, as shown by the low amount of leached Fe, XPS data showed an insignificant change of the surface before and after the reaction (Figure S2-SI). The latter findings suggest that the magnetite surface was not much modified at the end of the process. In analogy with previous results,[21] such issues suggest that the magnetic material may be recycled. Actually, there is evidence that magnetite induces effective photo-Fenton-like degradation of phenol in at least two consecutive cycles (see Figure S4-SI and related discussion).

References

(1) Wardman, P. Reduction potential of one-electron couples involving free radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637-1755.

(2) Neta, P.; Madhavan, V.; Zemel, H.; Fessenden, R. W. Rate constants and mechanism of reaction of $SO_4^{-\bullet}$ with aromatic compounds. *J. Am. Chem. Soc.* **1977**, *99*, 163-164.

(3) Elbenberger, H.; Steenken, S.; O'Neill, P.; Schulte-Frohlinde, D. Pulse radiolysis and electron spin resonance studies concerning the reaction of $SO_4^{-\bullet}$ with alcohols and ethers in aqueous solution. *J. Phys. Chem.* **1978**, *82*, 749-750.

(4) Liang, C.; Wang, Z.-S.; Bruell, C. J. Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere* **2007**, *66*, 106-113.

(5) Ahmad, M.; Teel, A. L.; Watts, R. J. Persulfate activation by subsurface minerals. *J. Contam. Hydrol.* **2010**, *115*, 34-45.

(6) Usman, M.; Faure, P.; Hanna, K.; Abdelmoula, M.; Ruby, C. Application of magnetite catalyzed chemical oxidation (Fenton-like and persulfate) for the remediation of oil hydrocarbon contamination. *Fuel* **2012**, *96*, 270-276.

(7) Neta, P.; Huie, R. E.; Ross, A. B. Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027-1284.

(8) Liang, C.; Bruell, C. J.; Marley, M. C.; Sperry, K. L. Persulfate oxidation for in situ remediation of TCE. II. Activated by chelated ferrous ion. *Chemosphere* **2004**, *55*, 1225-1233.

(9) Mora, V. C.; Rosso, J. A.; Carrillo Le Roux, G.; Mártire, D. O.; Gonzalez, M. C. Thermally activated peroxydisulfate in the presence of additives: A clean method for the degradation of pollutants. *Chemosphere* **2009**, *75*, 1405-1409.

(10) Anipsitakis, G. P.; Dionysiou, D. D. Radical generation by the interaction of transition metals with common oxidants. *Environ. Sci. Technol.* **2004**, *38*, 3705-3712.

(11) McElroy, W. J.; Waygood, S. J. Kinetics of the reactions of the SO_4^- radical with SO_4^-, $S_2O_8^{2-}$, H_2O and Fe^{2+}. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 2557-2564.

(12) Huang, W.; Brigante, M.; Wu, F.; Mousty, C.; Hanna, K.; Mailhot, G. Assessment of the Fe(III)-EDDS complex in Fenton-like processes: From the radical formation to the degradation of Bisphenol A. *Environ. Sci. Technol.* **2013**, *47*, 1952-1959.

(13) Magario, I.; Einschlag, F. S. G.; Rueda, E. H.; Zygadlo, J.; Ferreira, M. L. Mechanisms of radical generation in the removal of phenol derivatives and pigments using different Fe-based catalytic systems. *J. Mol. Catal. A-Chem.* **2012**, *352*, 1-20.

(14) Wang, Z. H.; Song, W. J.; Ma, W. H.; Zhao, J. C. Environmental photochemistry of iron complexes and their involvement in environmental chemical processes. *Prog. Chem.* **2012**, *24*, 423-432.

(15) Iurascu, B.; Siminiceanu, I.; Vione, D.; Vicente, M. A.; Gil, A. Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite. *Wat. Res.* **2009**, *43*, 1313-1322.

(16) Garrido-Ramirez, E. G.; Theng, B. K. G.; Mora, M. L. Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions - A review. *Appl. Clay Sci.* **2010**, *47*, 182-192.

(17) Do, S.-H.; Kwon, Y.-J.; Kong, S.-H. Effect of metal oxides on the reactivity of persulfate/Fe(II) in the remediation of diesel-contaminated soil and sand. *J. Hazard. Mater.* **2010**, *182*, 933-936.

(18) Usman, M.; Faure, P.; Ruby, C.; Hanna, K. Application of magnetite-activated persulfate oxidation for the degradation of PAHs in contaminated soils, *Chemosphere* **2012**, *87*, 234–240.

(19) Cornell, R. M.; Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrence, and Uses.* Wiley-VCH, NY, 2003.

(20) Watts, R. J.; Udell, M. D.; Kong, S. H.; Leung, S. W. Fenton-like soil remediation catalyzed by naturally occurring iron minerals. *Environ. Eng. Sci.* **1999**, *16*, 93-103.

(21) Xue, X.; Hanna, K.; Abdelmoula, M.; Deng, N. Adsorption and oxidation of PCP on the surface of magnetite: Kinetic experiments and spectroscopic investigations. *Appl. Catal. B - Environ.* **2009**, *89*, 432-440.

(22) Minella, M.; Marchetti, G.; De Laurentiis, E.; Maurino, V.; Minero, C.; Vione, D.; Hanna, K. Heterogeneous photo-Fenton oxidation with magnetite as iron source. *Appl. Catal. B - Environ.* **2014**, *155*, 102-109.

(23) Ndounla, J.; Kenfack, S.; Wethe, J.; Pulgarin, C. Relevant impact of irradiance (vs. dose) and evolution of pH and mineral nitrogen compounds during natural water disinfection by photo-Fenton in a solar CPC reactor. *Appl. Catal. B - Environ.* **2014**, *148*, 144-153.

(24) Groves, J. T. High-valent iron in chemical and biological oxidations. *J. Inorg. Biochem.* **2006**, *100*, 434-447.

(25) Minero, C.; Lucchiari, M.; Maurino, V.; Vione, D. A quantitative assessment of the production of $^\bullet OH$ and additional oxidants in the dark Fenton reaction: Fenton degradation of aromatic amines. *RSC Adv.* **2013**, *3*, 26443-26450.

(26) Usman, M.; Abdelmoula, M.; Hanna, K.; Grégoire, B.; Faure, P.; Ruby, C. Fe^{II} induced mineralogical transformations of ferric oxyhydroxides into magnetite of variable stoichiometry and morphology. *J. Solid State Chem.* **2012**, *194,* 328-335.

(27) Gorski, C.A.; Scherer, M. M. Determination of nanoparticulate magnetite stoichiometry by Mössbauer spectroscopy, acidic dissolution, and powder X-ray diffraction: A critical review. *Amer. Mineral.* **2010**, *95*, 1017-1026.

(28) Zegeye, A.; Abdelmoula, M.; Usman, M.; Hanna, K.; Ruby, C. In situ monitoring of lepidocrocite bioreduction and magnetite formation by reflection Mössbauer spectroscopy. *Amer. Mineral.* **2011**, *96,* 1410-1413.

(29) Gorski, C.A.; Scherer, M.M. Influence of magnetite stoichiometry on Fe^{II} uptake and nitrobenzene reduction. *Environ. Sci. Technol.* **2009**, *43*, 3675-3680.

(30) Romero, A.; Santos, A.; Vicente, F.; Gonzáles, C. Diuron abatement using activated persulphate: Effect of pH, Fe(II) and oxidant dosage. *Chem. Eng. J.* **2010**, *162*, 257-265.

(31) House, D. A. Kinetics and mechanism of oxidations by peroxydisulfate. *Chem. Rev.* **1962**, *62*, 185-203.

(32) Paczesniak, T.; Sobkowiak, A. The influence of solvent on the reaction between iron(II), (III) and hydrogen peroxide. *J. Mol. Catal. A-Chem.* **2003**, *194*, 1-11.

(33) Borer, P.; Sulzberger, B.; Hug, S. J.; Kraemer, S. M.; Kretzschmar, R. Photoreductive dissolution of iron(III) (hydr)oxides in the absence and presence of organic ligands: Experimental studies and kinetic modeling. *Environ. Sci. Technol.* **2009**, *43*, 1864-1870.

(34) Fu, H. B.; Cwiertny, D. M.; Carmichael, G. R.; Scherer, M. M.; Grassian, V. H. Photoreductive dissolution of Fe-containing mineral dust particles in acidic media. *J. Geophys. Res. - Atmos.* **2010**, *115*, D11304.

(35) Tang, J.; Myers, M.; Bosnick, K. A.; Brus, L. E. Magnetite Fe_3O_4 nanocrystals: Spectroscopic observation of aqueous oxidation kinetics. *J. Phys. Chem. B* **2003**, *107,* 7501-7506.

(36) Gallagher, K. J.; Feitknecht, W.; Mannweler, U. Mechanism of oxidation of magnetite to γ-Fe_2O_3. *Nature* **1968**, *217*, 1118-1121.

(37) Fang, J. Y.; Shang, C. Bromate formation from bromide oxidation by the UV/persulfate process. *Environ. Sci. Technol.* **2012**, *46*, 8976-8983.

(38) Ahmad, M.; Teel, A. L.; Furman, O. S.; Reed, J. I.; Watts, R. J. Oxidative and reductive pathways in iron-ethylenediaminetetraacetic acid-activated persulfate system. *J. Environ. Eng.* **2012**, *138*, 411-418.

(39) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}OH/O^{-\bullet}$) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513-886.

(40) Boukari, S. O.B.; Pellizzari, F.; Karpel Vel Leiter, N. Influence of persulfate ions on the removal of phenol in aqueous solution using electron beam irradiation. *J. Haz. Mat.* **2011**, *185*, 844-851.

(41) Gomis, J.; Vercher, R. F.; Amat, A. M.; Mártire, D. O.; González, M. C.; Bianco Prevot, A.; Montoneri, E.; Arques, A.; Carlos, L. Application of soluble bio-organic substances (SBO) as photocatalysts for wastewater treatment: Sensitizing effect and photo-Fenton-like process. *Catal. Today* **2013**, *209*, 176-180.

(42) Gonzalez-Olmos, R.; Holzer, F.; Kopinke, F. D.; Georgi, A. Indications of the reactive species in a heterogeneous Fenton-like reaction using Fe-containing zeolites. *Appl. Catal. A-Gen.* **2011**, *398*, 44-53.

(43) Enami, S.; Sakamoto, Y.; Colussi, A. J. Fenton chemistry at aqueous interfaces. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 623-628.

(44) Oztekin, R.; Sponza, D. T. Treatment of wastewaters from the olive mill industry by sonication. *J. Chem. Technol. Biotechnol.* **2013**, *88*, 212-225.

(45) De Luis, A. M.; Lombrana, J. I.; Menendez, A.; Sanz, J. Analysis of the toxicity of phenol solutions treated with H_2O_2/UV and H_2O_2/Fe oxidative systems. *Ind. Eng. Chem. Res.* **2011**, *50*, 1928-1937.

(46) Rizzo, L. Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment. *Wat. Res.* **2011**, *45*, 4311-4340.

(47) Kuo, C. Y.; Lo, S. L.; Chan, M. T. Oxidation of aqueous chlorophenols with photo-Fenton process. *J. Environ. Sci. Health Part B-Pestic. Contam. Agric. Wastes* **1998**, *33*, 723-747.

(48) Sun, Y. M.; Ren, X. H.; Cui, X. J.; Zhang, G. Q. The degradation mechanism of phenol induced by ozone in wastes system. *J. Molec. Mod.* **2012**, *18*, 3821-3830.

(49) Chen, J.; Eberlein, L.; Langford, C. H. Pathways of phenol and benzene photooxidation using TiO_2 supported on a zeolite. *J. Photochem. Photobiol. A - Chem.* **2002**, *148*, 183-189.

(50) Ahmed, M. M.; Barbati, S.; Doumenq, P.; Chiron, S. Sulfate radical anion oxidation of diclofenac and sulfamethoxazole for water decontamination. *Chem. Eng. J.* **2012**, *197*, 440-447.

(51) Ji, Y.; Ferronato, C.; Salvador, A.; Yang, X.; Chovelon, J. M. Degradation of ciprofloxacin and sulfamethoxazole by ferrous-activated persulfate: Implications for remediation of groundwater contaminated by antibiotics. *Sci. Total Environ.* **2014**, *472*, 800-808.

(52) Olmez-Hanci, T.; Arslan-Alaton, I. Comparison of sulfate and hydroxyl radical based advanced oxidation of phenol. *Chem. Eng. J.* **2013**, *224*, 10-16.

(53) Ahmed, M. M.; Chiron, S. Ciprofloxacin oxidation by UV-C activated peroxymonosulfate in wastewater. *J. Hazard. Mater.* **2014**, *265*, 41-46.

(54) Mack, J.; Bolton, J. R. Photochemistry of nitrite and nitrate in aqueous solution: A review. *J. Photochem. Photobiol. A - Chem.* **1999**, *128*, 1-13.

(55) Goldstein, S.; Rabani, J. Mechanism of nitrite formation by nitrate photolysis in aqueous solutions: The role of peroxynitrite, nitrogen dioxide, and hydroxyl radical. *J. Am. Chem. Soc.* **2007**, *129*, 10597-10601.

(56) Tan, C. Q.; Gao, N. Y.; Zhou, S. Q.; Xiao, Y. L.; Zhuang, Z. Z. Kinetic study of acetaminophen degradation by UV-based advanced oxidation processes. *Chem. Eng. J.* **2014**, *253*, 229-236.

1   **Table 1**. Some properties of the magnetite samples used in this study. XRD = X-Ray Diffraction, PZC = Point of Zero Charge, TEM =
2   Transmission Electron Microscopy, XPS = X-ray Photoelectron Spectroscopy.
3
4

Magnetite samples	Particle size range	SSA BET $(m^2\ g^{-1})$	PZC	Fe^{II}/Fe^{III} ratio	Remarks
S1	30-50 nm	75 ± 2	8.1	0.34± 0.02	Only magnetite (XRD), possibly maghemite traces (PZC, TEM), thin surface layer made up of Fe^{III} only (XPS)
S2	60-80 nm	26 ± 1	7.8	0.42± 0.02	Only magnetite (XRD), thin surface layer made up of Fe^{III} only (XPS)
S3	1-2 µm	1.7 ± 0.2	7.4	0.43 ± 0.02	Only magnetite (XRD)
S4	100-300 nm	8.5 ± 0.5	7.6	0.30 ± 0.02	Only magnetite (XRD)

5

6
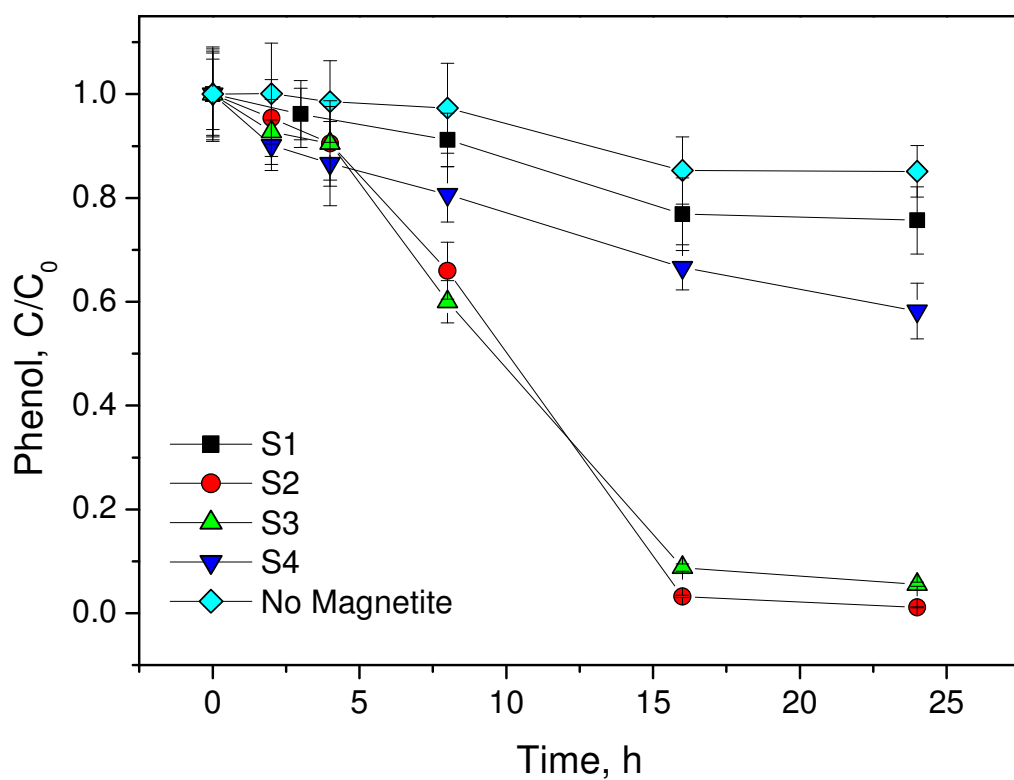
7

8

9   **Figure 1.** Time trend of 0.1 mM phenol under UVA irradiation with 0.5 mM $Na_2S_2O_8$, alone

10   or in the presence of 0.2 g L^{-1} magnetite (S1 to S4, initial pH ~5).

11

12

12
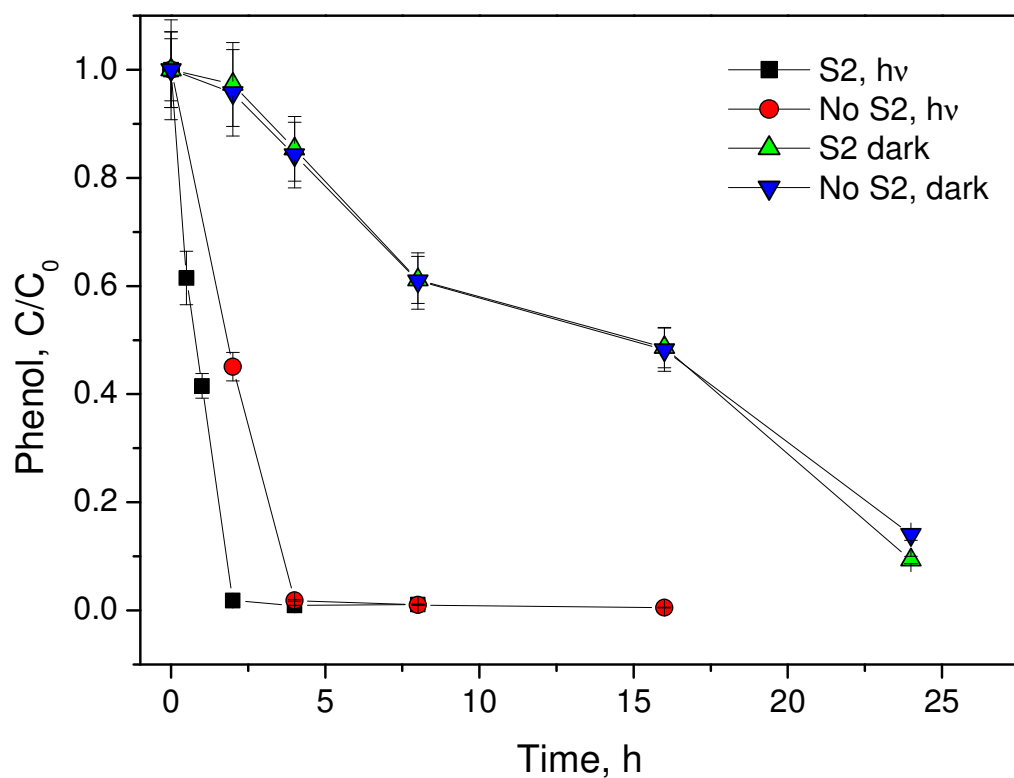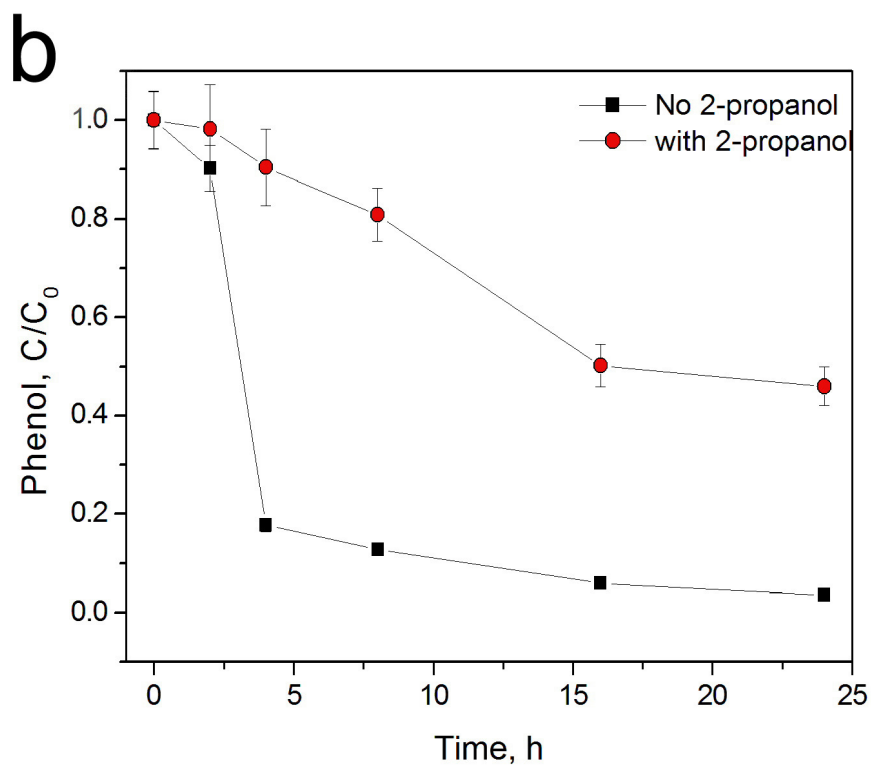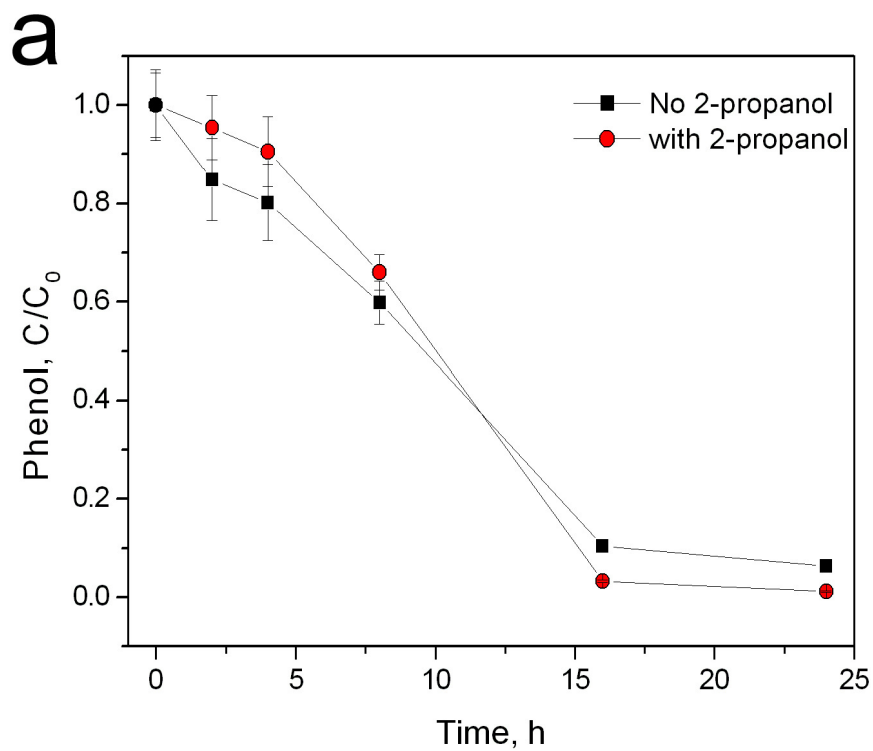

13
14
15   **Figure 2.** Time trend of 0.1 mM phenol under UVA irradiation (or in the dark) with 50 mM
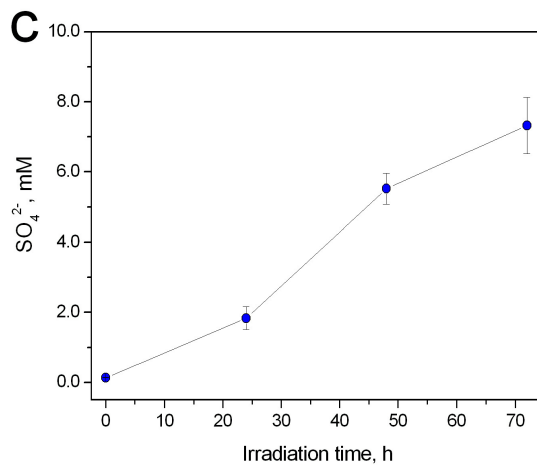16 $Na_2S_2O_8$, alone or in the presence of 0.2 g L^{-1} S2 (initial pH ~5).
17
18

a

b

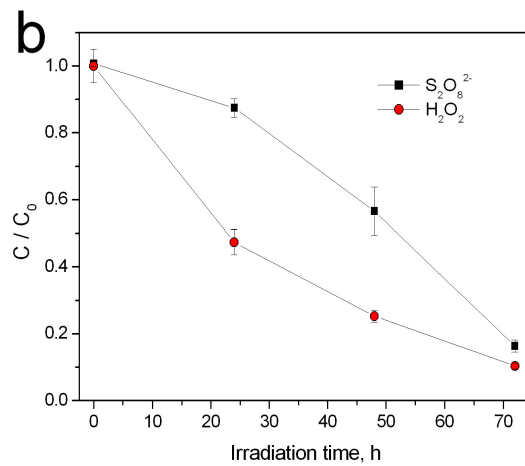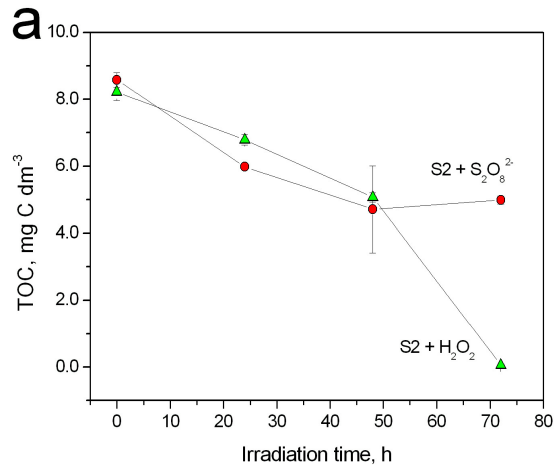18
19
20 **Figure 3.** Time trend of 0.1 mM phenol under UVA irradiation, with 0.2 g L^{-1} S2 and 0.5 mM
21   Na$_2$S$_2$O$_8$ **(a)** or 0.5 mM H$_2$O$_2$ **(b)**, in the presence and in the absence of 2 mM 2-
22   propanol. Initial pH ~5.
23

Figure 4. UVA irradiation of 0.1 mM phenol + 0.2 g L^{-1} S2, in the presence of 5 mM H$_2$O$_2$ or 5 mM Na$_2$S$_2$O$_8$. **(a)** Time trends of TOC. **(b)** Time trends of S$_2$O$_8^{2-}$ and H$_2$O$_2$. **(c)** Time trend of sulfate in the S$_2$O$_8^{2-}$ experiment.

23
24
25
26
27
28
29
30
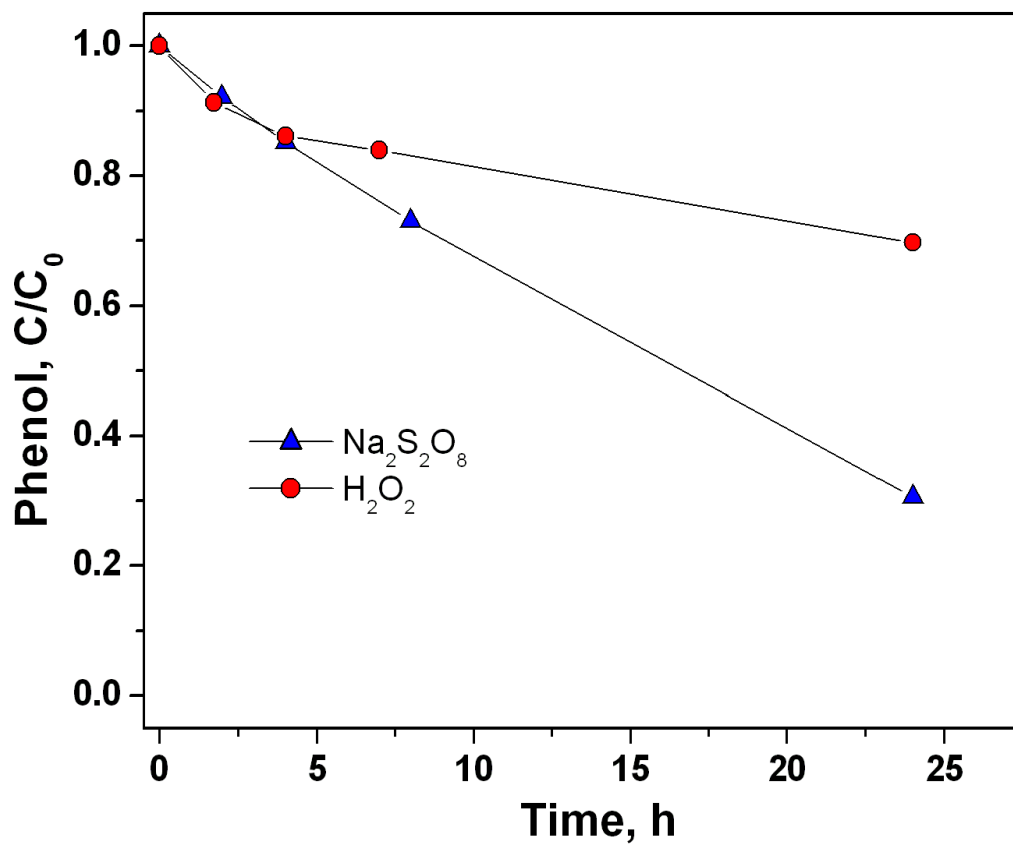
31
32
33 **Figure 5.** Time trend of 10 µM phenol under UVA irradiation with 0.2 g L^{-1} S2 and 0.5 mM
34   H_2O_2 or $Na_2S_2O_8$, in water sampled from Lake Candia (initial pH 8.3).
35