



## Evidence of singlet oxygen and hydroxyl radical formation in aqueous goethite suspension using spin-trapping electron paramagnetic resonance (EPR)

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### ABSTRACT

The generation of reactive species in an aqueous goethite suspension, under room light and aeration conditions, was investigated using the electron paramagnetic resonance (EPR) technique employing spin trap agents. The trap reagents, including 5,5-dimethylpyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP), were used for the detection of OH radicals (OH<sup>•</sup>) and singlet oxygen (<sup>1</sup>O<sub>2</sub>), respectively. On the addition of DMPO to the goethite suspended solution, a DMPO-OH adduct was formed, which was not decreased, even in the presence of the OH<sup>•</sup> scavenger, mannitol. This result implied a false positive interpretation from the DMPO-OH EPR signal. In the presence of TEMP reagent, a TEMP-O signal was detected, which was completely inhibited in the presence of the singlet oxygen scavenger, sodium azide. With both DMPO-OH and TEMP-O radicals in the presence and absence of radical scavengers, singlet oxygen was observed to be the key species formed in the room-light sensitized goethite suspension. In the goethite/H<sub>2</sub>O<sub>2</sub> system; however, both OH<sup>•</sup> and singlet oxygen were generated, with significant portions of DMPO-OH resulting from both OH<sup>•</sup> and singlet oxygen. In fact, the DMPO-OH resulting from OH<sup>•</sup> should be carefully calculated by correcting for the amount of DMPO-OH due to singlet oxygen. This study reports, for the first time, that the goethite suspensions may also act as a natural sensitizer, such as fulvic acids, to form singlet oxygen.

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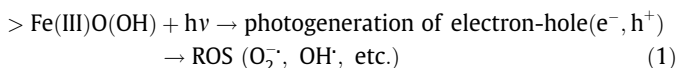
### 1. Introduction

Advanced Oxidation Processes (AOPs), which can eliminate pollutants at ambient temperature, based on the production of highly reactive intermediates, have shown great promise as effective methods for water treatment (Glaze et al., 1987; US EPA, 1998, 2001). In AOPs, hydroxyl radicals (OH<sup>•</sup>) are the most reactive intermediate contributing to the removal of target pollutants (Glaze et al., 1987; Buxton et al., 1988). Of the AOPs, heterogeneous types have been studied as a potential technology for soil remediation (Miller and Valentine, 1999; Liou and Lu, 2008). Some heterogeneous AOPs have been found to occur naturally on solid surfaces within aquatic systems (Paciolla et al., 1999), contributing in part to the self-purification of contaminated aquatic environments. Iron oxides are widespread within the natural environment and are among the most chemically reactive components of suspended matter in waters (Cunningham et al., 1988). Therefore, they can play important roles in the transformation or mobility of organic and inorganic molecules in aquatic systems. Recently, the use of iron(III) (hydr)oxides (goethite,  $\alpha$ -FeOOH and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) as heteroge-

neous catalysts for the effective oxidation of pollution matters by means of different oxidants has attracted great interest. Numerous papers have reported on the mechanism and application of iron oxide based Fenton-like processes as a very effective oxidation treatment of organic compounds (Lin and Gurol, 1996; Watts and Dilly, 1996; Lu, 2000; Andreozzi et al., 2002; Pham et al., 2009). Andreozzi et al. (2002) observed that the features of the system H<sub>2</sub>O<sub>2</sub>/goethite were due to the surface reaction between H<sub>2</sub>O<sub>2</sub> and adsorbed species. Ravikumar and Gurol (1994) and Miller and Valentine (1999) showed that naturally occurring iron oxides in soils were also capable of promoting Fenton-like reactions on the addition of hydrogen peroxide to soil slurry. Also, some papers have reported the possibility of the use of iron(III) (hydr)oxides for the photochemical oxidation of organic pollutants (Karametaxas et al., 1995; Mazellier and Bolte, 2000; Bandara et al., 2001; Andreozzi et al., 2003). Because iron(III) (hydr)oxides absorb light up to 600 nm, with most iron(III) (hydr)oxides and oxyhydroxides possessing semiconductor properties (Baumgarter et al., 1983; Mazellier and Bolte, 2000), under illumination this iron species can be used as photo-catalysts forming some ROS (reactive oxygen species), such as OH<sup>•</sup> or superoxide anion radicals, which could be responsible for the oxidative degradation reactions of environmental pollutants.

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Another important species that can be generated in nature by photosensitization is singlet oxygen,  $^1\text{O}_2$ . Currently, however, it is still very difficult to find a reliable method for the detection or isolation of key radical species, especially when various transient radical species are present.

Take  $\text{OH}^{\cdot}$  for instance, it can be directly observed using ultraviolet (UV) spectroscopy, but because of its weak UV absorption trace levels of  $\text{OH}^{\cdot}$  cannot be detected (Buhler et al., 1984; Sonntag, 2006). Eloviz and Gunten (1999) proposed an indirect method to detect and quantify  $\text{OH}^{\cdot}$  using *para*-chlorobenzoic acid (*p*-CBA) as an  $\text{OH}^{\cdot}$  probe and measuring the decay rate of *p*-CBA, with a known second-order rate constant value ( $k_{\text{OH}^{\cdot}, \text{pCBA}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). This indirect method also has an inherent weakness in the steady-state assumption, which is only applicable when  $\text{OH}^{\cdot}$  represents the primary radical and its quantity is sufficient to destroy the probe compound used. An alternative tool for the detection of free radicals is a spin-trapping method. In this method, radical trapping reagents are used to trap free radicals to yield stable reaction products, “spin adducts”, which can then be directly measured by electron paramagnetic resonance (EPR) spectroscopy. The spin trap, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), is widely used to identify free radicals, especially oxygen-centered radicals, such as superoxide anion, peroxy, and  $\text{OH}^{\cdot}$  (Janzen et al., 1980). However, Bilski et al. (1996) warned about the DMPO spin trap method for  $\text{OH}^{\cdot}$  detection, since besides direct the reaction path of  $\text{OH}^{\cdot}$  with DMPO, the spin trap DMPO can also be oxidized by other reactive species to yield DMPO-OH. They conducted their photochemical experiment in a homogeneous phase, using dyes as photosensitizer in an aqueous homogeneous solution. For the case of singlet oxygen detection, method of phosphorescence detection at 1270 nm was achieved by Krasnovsky (1976), and developed further by other several researchers including Schweitzer and Schmidt (2003) and Wu et al. (2011). However, low sensitivity due to weak signal of emission spectra is known to be a limitation for this method.

In this study, our aim was to observe the formation of reactive species, including  $\text{OH}^{\cdot}$ , in a goethite-mediated heterogeneous system to gain an understanding of the radical species involved in the self-purification mechanism of the soil surface and for future application of heterogeneous type AOPs for the removal of contaminants. Here, our focus was on the qualitative characteristics of reactive species identification employing the spin-trapping EPR method.

## 2. Experimental

### 2.1. Materials and method

The granular goethite, with 30–50 mesh, was purchased from Aldrich Chemical Co. The surface area was measured using a BET surface analyzer and found to be  $37 \text{ m}^2 \text{ g}^{-1}$ . 2,2,6,6-Tetramethyl-4-piperidone (TEMP, 95%) and sodium azide ( $\text{NaN}_3$ ) were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) (Aldrich Chemical Co., Milwaukee, WI, USA) was vacuum distilled and stored at  $-70^\circ\text{C}$  until used. All other chemicals were of reagent grade or better. All measurements were performed at room temperature.

All experiments were conducted in a 20 mL clear glass vial ( $\varnothing 25 \text{ mm} \times \text{H } 50 \text{ mm}$ ; diameter  $\times$  height), which was continuously stirred at a constant speed to provide complete mixing for uniform distribution and full suspension of the granular goethite. The aqueous goethite suspension was exposed to background ambient room

light radiation under a typical “cool white” fluorescent lamp (15c8 FL40EX-D, OSRAM, Ansan, Korea), which emits the visible spectrum having wavelength between 400 and 700 nm. The sample was sit from 1.9 m distance below from the set of two fluorescent lamps, which were fitted with an open reflector. The light intensity hitting the sample reactor could not be measured since the sample was also exposed to background ambient light. The light intensity hit on the sample laid table was measured to be 400–450 lx. Distilled water was prepared for all of the suspensions and solutions using a water purification system (Mill-Q, Millipore). All glassware was thoroughly washed with 0.1 M HCl and rinsed with distilled water before use. Reaction solutions were prepared by addition of an inorganic buffer (10 mM phosphate), with adjustment to the desired pH with NaOH or HCl. Hydrogen peroxide was measured using the horseradish peroxidase fluorometric method, with excitation and emission at 320 and 400 nm, respectively (Lazrus et al., 1985).

### 2.2. EPR measurements

A spin-trapping EPR technique, based on the method described by Utsumi et al. (1994), was employed. EPR spectra were recorded at 295 K with a Bruker EMX spectrometer, operated at 9.75 GHz, using a quartz capillary tube with a total volume 150  $\mu\text{L}$  in a TM 110. The trap reagent, DMPO (100 mM), was initially added into a solution containing goethite, with the solution continuously stirred using a magnetic bar for uniform mixing of the aqueous goethite suspended solution. Fifteen microlitre of the aliquot samples were taken at various time intervals and transferred into a capillary tube for EPR analysis. The EPR measurement was not affected by the solid suspension. A modulation frequency of 100 kHz, with a scan range and time of 8.0 mT and 180 s, respectively, and a microwave power of 5 mW and modulation amplitude of 0.1 mT were employed for the analysis. Also, the radical concentration was calculated by comparing the signal intensity with that of a standard solution of diphenyl-2-picrylhydrazyl (DPPH).

## 3. Results and discussion

### 3.1. EPR spectra of aqueous suspensions containing goethite

Under room light conditions, the EPR spectra were measured of the aqueous goethite suspensions containing 100 mM DMPO. The typical EPR signal of DMPO-OH is presented in Fig. 1, which shows the base line of the EPR spectrum, obtained from blank sample free of goethite (Fig. 1A), and Fig. 1B is the typical EPR spectrum obtained from the sample collected in the presence of goethite. The spectrum is composed of a quartet of lines, with a peak height ratio of 1:2:2:1, with parameters including hyperfine constants,  $a\text{N} = a\text{H} = 1.5 \text{ mT}$  and a  $g$ -value = 2.0055. These parameters exactly matched with typical DMPO-OH adduct EPR signal generated by the reaction of  $\text{OH}^{\cdot}$  with DMPO previously demonstrated (Utsumi et al., 1994; Han et al., 1998; Yoo et al., 2005).

### 3.2. Effect of goethite concentration

Fig. 2A shows the time course of DMPO-OH generation for various goethite concentrations from 1 to  $100 \text{ g L}^{-1}$ . The formation of DMPO-OH increased linearly with respect to a reaction time of 120 s, with a goethite mass range between 1 and  $50 \text{ g L}^{-1}$ . However, at the highest goethite concentration ( $100 \text{ g L}^{-1}$ ), the rate of DMPO-OH formation followed a rectangular hyperbola pattern of increase. This set of results clearly shows that the surface of goethite provides an active reaction site for the formation of a stable DMPO-OH adduct, with the parabolic increase at the highest goethite mass due

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