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Iron oxides semiconductors are efficients for solar water disinfection: A comparison with photo-Fenton processes at neutral pH

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ABSTRACT

The photocatalytic activities of four different commercially available iron (hydr)oxides semiconductors, *i.e.* hematite (α-Fe_2O_3), goethite (α-FeOOH), wüstite (FeO) and magnetite (Fe_3O_4), were evaluated for bacteria inactivation at neutral pH in the absence or presence of H_2O_2. Our results showed that heterogeneous photocatalysis and/or photo-Fenton processes catalyzed by low concentrations of reagents (0.6 mg/L Fe^{3+} and 10 mg/L H_2O_2) under sunlight may serve as a disinfection method for waterborne bacterial pathogens. In particular, we found that, with the exception of magnetite which need H_2O_2 as electron acceptor, all the other semiconductor iron (hydr)oxides were photoactive under sunlight in absence of H_2O_2 (using only oxygen as electron acceptor). Furthermore, for all iron (hydr)oxide studied in this work, no bacterial reactivation and/or growth was observed after photo-Fenton treatment. The same antimicrobial activity was obtained for the photocatalytic semiconducting action of hematite and goethite. Additionally, a delayed disinfection effect was observed to continue in the dark for the photo-assisted wüstite-based treatment. Electron spin resonance (ESR) in combination with spin-trapping was employed to detect reactive oxygen species (ROS) involved in heterogeneous photocatalysis and/or photo-Fenton treatments mediated by iron (hydr)oxide particles. In particular, ESR confirmed that $^{\bullet}OH$ and $O_2^{\bullet-}$ radicals were the principal ROS produced under photo-assisted action of iron (hydr)oxide particles in the absence or presence of H_2O_2. We also found that the components of natural water (*i.e.* natural organic matter (NOM) and inorganic substances) did not interfere with the photocatalytic semiconducting action of hematite to bacterial inactivation. However, these components enhance the bacterial inactivation by heterogeneous photo-Fenton action of hematite.

Overall our results demonstrated, for the first time, that low concentration of iron (hydr)oxides, acting both as photocatalytic semiconductors or catalysts of the heterogeneous photo-Fenton process at neutral pH, may provide a useful strategy for efficient bacterial disinfection.

1. Introduction

Drinking water scarcity is one of the most serious global challenges of our time [1,2]. The necessity for advanced water purification in terms of eliminating contaminants and killing bacteria will continue to increase, especially in developing countries where water treatment is often inadequate or non-existent. The photo-assisted Fenton oxidation is one of the most popular and widely studied advanced oxidation processes (AOPs). In particular, photo-Fenton reactions play a key role in sunlight-assisted AOPs due to the fact that they take advantage of UV, near-UV and visible light up to 600 nm, thus comprising 35% of the total energy coming from the solar spectrum. Until now, the pH of the process was generally perceived as the limiting factor for photo-Fenton systems, because $Fe(OH)^{2+}$, *i.e.* the most photo-active Fe^{3+}-hydroxy complex under UV-A and visible solar light, is predominant at low pH (~2.8) [3,4]. However, recently, the photo-inactivation of *E. coli* by photo-Fenton system at near neutral pH has been reported [5–10]. A near neutral pH, a spontaneous chemical oxidation of ferrous ions to ferric by dissolved oxygen in water occurs, involving a variety of partially oxidized meta-stable ferrous–ferric intermediate species (*e.g.* green rusts). These iron intermediates ultimately transform

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into a variety of stable iron oxide end-products such as hematite, magnetite, goethite and lepidocrocite [11,12].

Recent researches haves focused on the idea of replacing dissolved iron with solid catalysts in so-called heterogeneous Fenton reactions. In particular, quite a number of iron-containing systems have been developed for organic pollutants degradation, including iron oxides [13–15], iron-immobilized materials [16–18], clays and carbon materials [19,20], *etc.*

Iron oxides are among the most chemically reactive components of suspended matter in aquatic systems and can be easily prepared in laboratory conditions [21]. Additionally, they are considered non-toxic and environmentally friendly compounds, similarly to free iron ions [22]. Most of them reveal semiconductor properties and then may also act as photocatalysts, even though their overall efficacy can be impaired by a very efficient hole–electron recombination [23].

Possible semiconducting mechanisms involved in iron oxide can be summarized as follows. In the first step, a photon with energy equal to or greater than the material's band gap, which separates the conductance band (CB) and valence band (VB), is absorbed by a semiconducting particle of iron oxide. This gives rise to the generation of the electron/hole pair (Eq. (1)). Although the excited electron/hole pair can recombine and release the energy as heat, some of the excited electrons and holes can contribute to redox reactions on the surface of a semiconducting particle of iron oxide. The most relevant redox processes, which take place after the photo-generation of electrons (e^-_{cb}) and holes (h^+_{vb}) in semiconducting particles of iron oxide suspended in aqueous medium, containing also an organic substance (RX), are summarized in Eqs. (1)–(5) [21]. ($>Fe^{2+}$ and $>Fe^{3+}$ represent the Fe^{2+}/Fe^{3+} species in solid or solution phase).

$$Fe_2O_3 + h\nu \rightarrow Fe_2O_3\,(e^- + h^+) \quad (1)$$

$$e^-_{(cb)} + O_2 \rightarrow O_2^{\bullet -} \quad (2)$$

$$h^+_{(vb)} + O_2^{\bullet -} \rightarrow {}^1O_2 \quad (3)$$

$$e^-_{(cb)} + {>}Fe^{3+} \rightarrow {>}Fe^{2+} \quad (4)$$

$$h^+_{(vb)} + RX_{ad} \rightarrow RX_{ad}^{\bullet +} \quad (5)$$

Irradiation may also enhance the heterogeneous Fenton process on iron-bearing particles, by promoting the photo-reduction of $>Fe^{3+}OH$ to $>Fe^{2+}$ (Eq. (6)), which subsequently reacts with H_2O_2 generating $^\bullet OH$ radicals at the particle surface (Eq. (7)).

$${>}Fe^{3+}OH + h\nu \rightarrow {>}Fe^{2+} + {}^\bullet OH \quad (6)$$

$${>}Fe^{2+} + H_2O_2 \rightarrow {>}Fe^{3+} + OH^- + {}^\bullet OH \quad (7)$$

A large number of studies have demonstrated that iron oxide minerals such as magnetite, hematite, goethite or ferrihydrite are effective for oxidation of organic pollutants and compounds that affect water quality [13,14,24–26]. However, since little research has been conducted on these compounds towards inactivation of microorganisms present in aqueous solutions [7,17,27–29], their role in bacterial inactivation is not well known. In our previous paper [7], it was shown that goethite was efficiently inactivating bacteria, acting as semiconductor *via* a photocatalytic process and as an heterogeneous iron source in Fenton process around neutral pH.

In this work, the bacterial inactivation by addition of $FeSO_4$ in illuminated water at initial pH of 6.5 and 7.5 were compared in the absence or presence of H_2O_2. Also, the ferric precipitates formed during the treatments were identified.

The main purpose of this work was to investigate the disinfection ability of four iron (hydr)oxides in aqueous media under solar light illumination, at near-neutral pH of 6.5, in the absence or presence of H_2O_2, to better distinguish their action mode, either as semiconductors or as iron source in heterogeneous photo-Fenton processes. The iron (hydr)oxide (hematite, goethite, wüstite and magnetite) used in this study are the most common constituents of the sub-surface environment. Furthermore, reactive oxygen species (ROS) generated by iron (hydr)oxides during these processes were identified and quantified. Finally, the influence of natural organic matter (NOM) on the activity of hematite during bacterial inactivation was evaluated.

2. Materials and methods

2.1. Chemicals

Ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$) (Riedel-de Haën 99–103.4%), hydrogen peroxide (H_2O_2) 30% w/v (Riedel de Haën). Sodium hydroxide (NaOH, 98%) and hydrochloric acid (HCl, 36.5%), were purchased from Sigma-Aldrich. The spin-trap, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), was purchased from Enzo Life Sciences (ELS) AG (Lausen, Switzerland). The spin probes, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) and 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPONE), as well as their respective precursors, *i.e.* 2,2,6,6-tetramethyl-4-piperidinol (TMP-OH) and 2,2,6,6-tetramethyl-4-piperidone (TEMPONE precursor), were purchased from Sigma Aldrich (Buchs, Switzerland). The commercially available iron (hydr)oxides particles, *i.e.* goethite, hematite, wüstite, and magnetite, were purchased from Sigma-Aldrich. The particles size were (<50 mesh and <5 μm). The most relevant physicochemical properties of these iron (hydr)oxides particles are shown in Table 1.

All solutions were prepared immediately prior to irradiation with the use of Milli-Q water (18.2 MΩ-cm). Two different types of water were used to suspend bacteria that are Milli-Q water and natural water from the Geneva Lake. Table 2 shows the physicochemical characteristics of these waters.

2.2. Bacterial strains and growth media

The bacterial strain used was *E. coli* K12 (MG1655), a non-pathogenic wild-type strain, which can be handled with little genetic manipulation. Bacteria was inoculated from a stock in a

Table 1
Physicochemical properties of the particles studied.

Iron minerals	Formula	Iron oxidation state	Surface area (m^2/g)[a]	IEP[b]	Band gap energy[b] (eV)
Goethite	α-FeOOH	+3	37.0	7.5–8.5	2.1
Hematite	α-Fe_2O_3	+3	–	8.5	2.2
Wüstite	FeO	+2	10.0	8.0	2.4
Magnetite	Fe_3O_4	+2, +3	2.0	6.0–6.5	0.1

[a] Surface area reported by the manufacturer and from references [14,66].
[b] Isoelectric point and band gap energy, from references [21,60].

Table 2
Physicochemical characteristics of the waters used in the experiments.

Parameter	Milli-Q water	Geneve lake water
Conductivity at 20 °C (μS/cm)	<0.055	252
Transmittance at 254 nm (%)	100	96
pH	6.5	7.9
Total organic carbon (TOC) (mg C/L)	<0.005	0.8–1
Iron (mg/L)	–	0.019
Phosphates	–	0.012
Hydrogen carbonate (mg CO_3^-/L)	–	108
Chloride mg Cl^-/L)	–	8.0
Sulfate (mg SO_4^{-2}/L)	–	48
Nitrate (mg NO_3^-/L)	–	2.7