Applied Catalysis B: Environmental 154–155 (2014) 102–109

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Photo-Fenton oxidation of phenol with magnetite as iron source

Marco Minella [a], Giulia Marchetti [a], Elisa De Laurentiis [a], Mery Malandrino [a], Valter Maurino [a], Claudio Minero [a], Davide Vione [a,*], Khalil Hanna [b,c,**]

[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
[c] Université Européenne de Bretagne, France

ARTICLE INFO

Article history:
Received 4 September 2013
Received in revised form 28 January 2014
Accepted 4 February 2014
Available online 13 February 2014

Keywords:
Photo-Fenton
Magnetite
Advanced oxidations process
Heterogeneous photo-Fenton oxidation

ABSTRACT

In this work, magnetite-catalyzed Fenton reaction was investigated under UVA irradiation for the degradation of phenol as model compound. Four kinds of magnetite were used having different particle size, surface area and Fe^{II} content. Different kinetic behaviors were observed, thereby underscoring the strong implications of surface and chemical properties of magnetite. The size and surface area of the particles seemed to be less important, while the Fe^{II}/Fe^{III} ratio played some role. Despite the link between magnetite reactivity and its structural Fe^{II} content, light-induced reduction of Fe^{III} to Fe^{II} was found necessary to promote the Fenton-based reactions. As surface Fe^{II} may be oxidized or otherwise unavailable, initial photoactivation may be needed to trigger the Fenton reactivity. Two major driving forces were highlighted that account for the photoactivity of magnetite at pH 3: (i) the formation of intermediates such as hydroquinone that are able to reduce Fe^{III} to Fe^{II}, and (ii) the accumulation of dissolved Fe due to magnetite dissolution, both in dark and under irradiation. Very interestingly, the photo-Fenton degradation of phenol was also observed under neutral conditions. In this case, for two out of four samples, the degradation rates were quite near those found at pH 3, which is usually reported as the optimum pH value of the process. The magnetite ability to promote photo-Fenton reactions even under circumneutral pH conditions, the limited iron leaching and its easy magnetic separation makes magnetite a promising catalyst in wastewater treatment applications.

1. Introduction

The classic Fenton process involves aqueous ferrous ions and H_2O_2 that react together to form $^{\bullet}OH$, in a reaction that can be expressed as follows (in acidic solution, Fe^{II} is usually present as Fe^{2+} and Fe^{III} may be present as $FeOH^{2+}$) [1]:

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III} + OH^- + {}^{\bullet}OH \qquad (1)$$

Reaction (1) is a stoichiometric process, but Fe is often used in catalytic amount because of the subsequent pathways of H_2O_2 decomposition [2], which regenerate Fe^{II} that reacts again in (1). The classical Haber–Weiss view of the process reads as follows [3]:

$$FeOH^{2+} + H_2O_2 \rightarrow Fe^{II} + HO_2^{\bullet} + H_2O \qquad (2)$$

$$FeOH^{2+} + HO_2^{\bullet} \rightarrow Fe^{II} + O_2 + H_2O \qquad (3)$$

The production of $^{\bullet}OH$, a powerful reactant that is able to degrade a wide variety of xenobiotics at diffusion-limited reaction rates, accounts for the widespread use of the Fenton reaction among advanced oxidation processes (AOPs) for the abatement of recalcitrant compounds in water and wastewater. Reaction (1) is the fast step of the Fenton process, while reactions (2) and (3) are considerably slower. Therefore, when Fe^{II} and H_2O_2 are mixed in the presence of a pollutant, one often observes a very fast first step followed by a considerable slowing down of the reaction. This issue complicates the use of Fe^{III}, which is much cheaper than Fe^{II} in the classic Fenton process. It also explains why several variants of the Fenton reaction have been proposed. An example is the photo-Fenton process, where the formation of Fe^{II} from Fe^{III} takes place photochemically (L in reaction (5) is an organic ligand such as oxalate) [4,5]:

$$FeOH^{2+} + h\nu \rightarrow Fe^{II} + {}^{\bullet}OH \qquad (4)$$

$$Fe^{III}\text{-}L + h\nu \rightarrow Fe^{II} + L^{+\bullet} \qquad (5)$$

The Fenton reaction is usually carried out in acidic conditions (optimum pH is 3), not only to keep Fe^{III} dissolved but mostly

---

* Corresponding author at: Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 5, 10125 Torino, Italy. Tel.: +39 011 6705296.
** Corresponding author at: Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France.
Tel.: +33 02 23238027.
E-mail addresses: davide.vione@unito.it (D. Vione), khalil.hanna@ensc-rennes.fr (K. Hanna).

http://dx.doi.org/10.1016/j.apcatb.2014.02.006
0926-3373/© 2014 Elsevier B.V. All rights reserved.

because the $^{\bullet}OH$ generation in reaction (1) has maximum effectiveness in an acidic environment. Furthermore, among the Fe^{III} species, the $FeOH^{2+}$ hydroxocomplex that prevails at pH 3 has the highest reactivity toward reduction by H_2O_2 and $HO_2^{\bullet}$ in reactions (2) and (3) [2,3,6]. The pH effect is a major issue where the still unresolved complexity of the Fenton mechanism comes to the surface, behind the apparent straightforwardness of reactions (1)–(5). Indeed, reaction (1) actually involves the formation of a highly oxidized Fe adduct, often indicated as ferryl (*e.g.* ferryl ion FeO^{2+}), which does not necessarily evolve into $^{\bullet}OH$ [1,7,8]. The $^{\bullet}OH$ formation is most effective (but by no means quantitative) at pH 3 and it usually decreases at higher or lower pH values [2,3]. Therefore, it is not surprising to find differences between the Fenton process and the expected reactivity of $^{\bullet}OH$ [1,7,9].

Recently, magnetite ($Fe^{II}Fe_2{}^{III}O_4$, Fe^{II}–Fe^{III} mixed valence oxide) was successfully used as iron source in heterogeneous Fenton reactions, because Fe^{II} plays an important role in the initiation of the Fenton process according to the classical Haber–Weiss mechanism. Magnetite, pristine, doped or coupled with other oxides (*e.g.* CeO_2) was shown to effectively catalyze the oxidative degradation of target compounds at circumneutral pH. It also exhibited good structural stability and excellent reusability [10–19]. Magnetite can be synthesized in the laboratory by various biotic and abiotic pathways. Abiotic procedures to form magnetite include co-precipitation of soluble Fe^{II} and Fe^{III} species, oxidation of hydroxylated Fe^{II} species and ferric oxides transformation [20–24]. The morphology, crystallography and specific surface area of natural or synthetic magnetite can vary widely [25,26]. Similarly to other iron oxides, magnetite exists as micrometric and nanometric particles in many natural and engineered environments. Because the specific surface area of nanosized particles is very large, their surface reactivity is exalted and they can play a potentially pre-eminent role in sorption and/or redox processes.

The heterogeneous photo-Fenton reaction can solve the problem of eliminating and re-using Fe from the reaction system at the end of the process, but the separation of the solid phase is still an open issue. The separation problem is even more important in the case of oxide nanoparticles, which are potentially more reactive because of the favorable surface-to-volume ratio. From this point of view, the fact that magnetite undergoes very easy magnetic separation from aqueous systems makes it a very interesting material to be tested for photo-Fenton reactivity. Moreover, it is very interesting to check whether, as for dark reactivity, the photo-activity of magnetite is maintained under circumneutral pH conditions, which would overcome the need of pH adjustment. At circumneutral pH the operational mechanism of the photo-Fenton process is still controversial, in particular in the presence of organic ligands for iron (EDTA, humic acids...) [27,28]. Quite surprisingly, very few data are available about the use of magnetite in photo-Fenton chemistry. To fill in this knowledge gap, the present work has the goal of studying the photo-Fenton reactivity of magnetite toward the degradation of phenol. The latter was chosen because it is a substrate of well-known behavior and it can be very helpful in the elucidation of reaction pathways [29].

The photo-Fenton reactivity of magnetite could depend on characteristics and surface properties such as crystallinity, surface area, Fe^{II} content or Fe^{II}/Fe^{III} structural ratio. For this reason, dark and irradiation experiments were carried out with four different kinds of magnetite (two synthetic and two commercial) having different morphologies and structural properties. The aim was to point out the effects of particle size, surface area and Fe speciation on the magnetite ability to promote heterogeneous Fenton or photo-Fenton reactions, a topic that has attracted very little attention in the literature to date. Phenol was chosen as model compound in this study because of its well-known photo-Fenton degradation, which considerably aids in the understanding of the reaction pathways [30,31].

2. Experimental

2.1. Reagents and materials

Phenol (purity grade 99%), 1,10-phenanthroline (99%), hydroquinone (98%), H_3PO_4 (85%), $HClO_4$ (70%), magnetite (97%) and methanol (gradient grade) were purchased from Aldrich, magnetite (98%) from Prolabo, H_2O_2 (35%) from VWR International. All reagents were used as received, without further purification. The aqueous solutions were prepared by using water of Milli-Q purity (TOC < 2 ppb, resistivity ≥18.2 mΩ cm).

2.2. Synthesis of magnetite samples

Experiments were conducted with four different kinds of magnetite. Among them, two (S1 and S2) were prepared in the lab from two different Fe(III)-oxyhydroxides, the third one (S3) was purchased from Prolabo and the fourth (S4) from Aldrich. S1 and S2 were prepared by starting from 2-line ferrihydrite and lepidocrocite (γ-FeOOH), respectively. The ferrihydrite and lepidocrocite were synthesized as explained in previous work [32], according to the methods proposed by Schwertmann and Cornell [33]. All the Fe^{III} precipitates were washed several times to remove electrolytes, centrifuged and then dried. Starting from these materials, S1 and S2 were then prepared by Fe^{II}-induced mineralogical transformations of synthetic ferric oxyhydroxides, as explained in detail in previous works [32,34,35]. The suspensions were vigorously stirred for two days, they were then centrifuged and the solid was dried in a glove box.

2.3. Sample characterization

To identify the crystal structure of minerals, the solid samples were analyzed by X-ray powder diffraction (XRD). The XRD data were collected with a D8 Bruker diffractometer, equipped with a monochromator and a position-sensitive detector. The X-ray source was a Co anode (λ = 0.17902 nm). The diffractogram was recorded in the 3–64° 2θ range, with a 0.0359° step size and a collection time of 3 s per point.

Transmission Electron Microscopy (TEM) analysis was also performed to obtain information regarding morphology, size, shape and arrangement of particles. TEM observations were carried out with a Philips CS20 TEM (200 kV) coupled with an EDAX energy dispersive X-ray spectrometer. The solid powder was re-suspended in 2 mL ethanol under ultrasonication and a drop of the suspension was evaporated on a carbon-coated copper grid, which was placed on filter paper for analysis.

The specific surface area of the iron oxides was determined by multipoint N_2–BET analysis, using a Coulter (SA 3100) surface area analyzer. The point of zero charge (PZC) of the tested magnetites was determined by potentiometric titration of the oxides in a thermostatic double-walled Pyrex cell at 293 K in 0.001, 0.01 and 0.1 M NaCl solutions, according to the method of Parks and de Dyne [36]. The N_2 gas was constantly passed through the suspensions to bubble out CO_2. The pH value of the suspensions was adjusted with titrant solutions (HCl or NaOH) and recorded with an Orion pH meter model 710A, connected to a combined glass electrode. Blank titrations were also performed with similar solutions in the absence of solid.

The Fe^{II} content in the oxide structure was determined by chemical analysis after acid dissolution with 6 M HCl. Ferrous and total iron concentrations were determined using a modified 1,10-phenanthroline method [37]. The Fe^{II}/Fe^{III} ratios of oxides are