Mixed iron oxides as Fenton catalysts for gallic acid removal from aqueous solutions

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ABSTRACT

A study was conducted on the behavior as Fenton catalysts of three commercial mixed iron oxides: copper ferrite, magnetite, and ilmenite, using H_2O_2 for the degradation and mineralization of gallic acid (GA) at temperatures between 15 and 35 °C and pH of 4.3. Investigation of the activity of the catalysts was complemented by study of the metal ion leaching under reaction conditions. GA was completely mineralized with the three mixed iron oxides in the following order of catalytic activity: $CuFe_2O_4 > Fe_3O_4 > FeTiO_3$, and the ferrites could be quickly and completely separated after the reaction by a magnetic field. According to these results, there appears to be a synergic effect between Cu and Fe ions placed in octahedral sites, and Cu ions may be the main active sites for HO• radical generation. The efficiency of H_2O_2 utilization followed the inverse order of the catalytic activity of the mixed iron oxides, likely because the excess hydroxyl radicals generated during the reaction were quenched by hydrogen peroxide, yielding the less reactive hydroperoxide radicals. A very large amount of Cu and Fe ions leached from copper ferrite and decreased at higher reaction temperatures. These leached ions also acted as homogeneous Fenton catalysts in GA degradation and mineralization. A much lower amount of Fe ions was leached from magnetite and ilmenite in comparison to copper ferrite. From the perspective of long-term applications, magnetite with intermediate catalytic activity but with higher efficiency and much lower Fe ion leaching in comparison to copper ferrite may be more appropriate for GA removal.

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1. Introduction

Advanced oxidation processes (AOPs) are applied in the treatment of different wastewaters to remove recalcitrant organic pollutants for environmental remediation. They operate at near-ambient temperature and pressure and are characterized by the generation of hydroxyl radicals, HO•. These potent (E° = 2.8 V) and non-selective oxidants can oxidize and mineralize organic pollutants in water, yielding CO_2 and other inorganic compounds [1–3]. The Fenton process is one of the most cost-effective AOPs and is based in the decomposition of H_2O_2 by Fe^{2+} ions under acidic conditions according to Eq. (1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO• \tag{1}$$
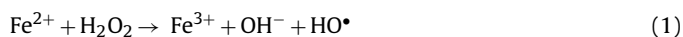
Fe^{3+} ions then react with H_2O_2 to regenerate Fe^{2+} ions according to Eq. (2)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2• \tag{2}$$
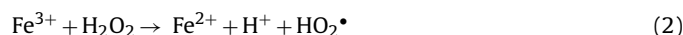
When the reaction is initiated by Fe^{3+} ions, the process is generally known as Fenton-like, although it is a cycle, and both ions are simultaneously present regardless of the starting iron ions. Eqs. (1) and (2) are commonly used to describe the Fenton oxidation, although the process is much more complex and includes many other reactions [3–5].

Other transition metal ions can act as Fenton-like catalysts [6]. Thus, Cu^+ ions can generate HO• radicals according to Eq. (3)

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + HO• \tag{3}$$

A reduction mechanism similar to that of Fe^{3+} ions has been reported for Cu^{2+} ions [6], Eq. (4)

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + H^+ + HO_2• \tag{4}$$
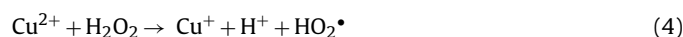
In addition, the hydroperoxide radical, $HO_2•$, can also reduce oxidized forms of the metal cations, Eqs. (5) and (6)

$$Fe^{3+} + HO_2• \rightarrow Fe^{2+} + H^+ + O_2 \tag{5}$$

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$$Cu^{2+} + HO_2^\bullet \rightarrow Cu^+ + H^+ + O_2 \qquad (6)$$

Mixed iron oxides such as ferrites and ilmenite have been applied as heterogeneous catalysts in Fenton-like processes [3,7–14]. The formula of ferrites is MFe_2O_4, where M is a divalent cation such as Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, etc. They are all inverse spinel, either totally or partially, with the oxide ions forming a face-centered cubic-close packed array and leaving tetrahedral (A) and octahedral (B) coordination sites [15]. In all inverse spinels, M^{2+} ions occupy B sites, whereas Fe^{3+} ions are equally divided between A and B sites in total inverse spinels and unequally divided between A and B sites in partial inverse spinels.

In spinel powders, B sites are almost exclusively exposed on the surface and are the only active catalytic sites [16]. Furthermore, all ferrites are ferrimagnetic [17] and can therefore be readily separated from the reaction phase by applying a magnetic field. These characteristics of spinels make them better catalysts in comparison to other iron oxides and conventional Fe-supported catalysts in AOPs. Thus, magnetite can accommodate both Fe(II) and Fe(III) ions at B sites, which can be reversibly oxidized and reduced while preserving the same structure. This is a ubiquitous mineral in the Earth's crust, and the iron cations can frequently be isomorphically substituted by divalent, trivalent, and tetravalent cations while maintaining the same structure [18]. Some substitutions improve the catalytic properties of magnetite in AOPs of organic pollutants. One of these ferrites is $CuFe_2O_4$, which has proven to be a potent material for the catalytic activation of peroxides such as hydrogen peroxide and peroxymonosulfate [9–11,13].

Ilmenite ($FeTiO_3$) is one of the main TiO_2-containing minerals, and its structure is very similar to that of corundum, with a close-packed hexagonal array of oxygen ions but with two different cations, Fe^{2+} and Ti^{4+}, which occupy two-thirds of octahedral sites in alternate layers [17]. Ilmenite possesses paramagnetic properties [17].

The objective of this study was to compare the behavior as Fenton catalysts of three mixed iron oxides, copper ferrite, magnetite and ilmenite, using H_2O_2 for the degradation and mineralization of GA (3,4,5-trihydroxybenzoic acid) at temperatures between 15 and 35 °C and pH 4.3. GA is present in natural waters from the decay of vegetation and is abundant in agro-industry wastewater effluents, being considered a model polyphenol compound [19–21]. Examination of the activity of these catalysts in the oxidation reaction of GA was complemented by study of the leaching of the metal ions under reaction conditions, key data for the integrity of the catalysts and of major importance for long-term applications and from an environmental standpoint.

2. Experimental

2.1. Materials

The mixed iron oxides $CuFe_2O_4$, Fe_3O_4, and $FeTiO_3$ used as Fenton catalysts were supplied by Sigma Aldrich with a purity of 98.5, 95.0, and 99.9%, respectively. GA, H_2O_2 (30 wt%), $Fe_2(SO_4)_3 \cdot nH_2O$, $CuSO_4 \cdot 5H_2O$, and CH_3-COOH were also supplied by Sigma Aldrich (reagent grade) and were used as-received with no further purification.

2.2. Characterization methods

GA was characterized by potentiometric titration to determine its speciation diagram as a function of the pH, depicted in Fig. S1 (Supplementary data). The diagram shows the distribution of neutral, anionic, and cationic forms in aqueous medium at different pH values [22].

Various techniques were employed to characterize the catalysts, which were as-received (fresh) and, in some cases, previously used in Fenton reaction at 35 °C for 1 h. Their morphology was examined by SEM using Carl Zeiss SMT equipment; power X-ray XRD patterns were established with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation; and the surface area, S_{BET}, was estimated by applying the BET equation to N_2 adsorption isotherms at −196 °C, which were obtained with an Autosorb 1 from Quantachrome. Fig. S2 depicts the pH at the point of zero charge (pH_{PZC}) of the mixed iron oxides, which was determined by potentiometric titration [23]. XPS was performed using the Escalab 200R system (VG Scientific Co.) equipped with MgK_α X-ray source (hγ = 1253.6 eV) and hemispherical electron analyzer. The internal standard peak to determine binding energies (BEs) was the C_{1s} peak at 284.6 eV, used to obtain the number of components, position of the peaks, and peak areas.

A SQUID magnetometer (Quantum Design model MPMS-XL) was used to record at room temperature the magnetization (M) of samples as a function of the magnetic field applied (H). M−H curves describe the magnetic response of the materials and permit measurement of the saturation and remnant magnetization, M_S and M_R, respectively, as well as the coercivity, H_C.

2.3. Fenton reaction

The Fenton reaction was carried out in conical flasks containing 0.2 L of reaction solution that were thermostated between 15 and 35 °C and shaken at 300 rpm. In all cases, GA and H_2O_2 concentrations were 0.12 and 2.64 mM, respectively, and the amount of catalyst was 50 mg L^{-1}. The dose of H_2O_2 used was almost two-fold higher than the stoichiometric amount (1.44 mM) for complete oxidation of GA to CO_2 and H_2O. The initial pH was 4.3, which resulted from the ingredients used in the suspension, and the final pH was 4.0 for the ferrites and 4.2 for the ilmenite. Hence, the pH was practically unchanged during the reaction. The experimental procedure was as follows: first, the catalyst was added to the GA solution and the suspension was thermostated to the required temperature; then, the Fenton reaction was initiated by adding H_2O_2 to the suspension. Each data point for GA removal kinetics was obtained from a different flask. Suspensions were analyzed immediately after filtering through 0.22 μm nylon membranes.

GA concentrations were measured by HPLC (Thermo-Fisher) equipped with a UV8000 photodiode detector, using a Hypersil Gold (250 × 4.6 mm) chromatographic column. The mobile phase was a mixture of 10% HPLC grade methanol and 90% ultrapure water (0.1% formic acid) in isocratic mode at a flow of 1 mL min^{-1}. The detector wavelength was 260 nm. In addition, GA mineralization was evaluated by measuring the TOC with a TOC-5000A model Shimadzu analyzer. TOC results were the average of at least three measurements with an accuracy of ±5%. The residual H_2O_2 concentration in solution was determined by the ammonium heptamolybdate method [24]. Metal ion leaching from the catalysts was determined by atomic absorption spectrometry.

The HO$^\bullet$ radicals generated and consumed in the Fenton processes at different reaction times were quantitatively measured using a previously described method for their determination in AOPs [25]. For this purpose, dimethyl sulfoxide was added to trap the HO$^\bullet$ radicals in solution, quantitatively producing formaldehyde that then reacted with 2,4-dinitrophenylhydrazine to form the corresponding hydrazone, which was analyzed by HPLC.

Concentrations of oxalic and formic acid (obtained as degradation products) were followed as a function of reaction time by ionic chromatography using a Dionex DX-120 equipped with an AS9-HC column and a conductivity detector with suppressor device. The mobile phase was 3.8 mM $NaHCO_3$ and 3.0 mM Na_2CO_3 at a flow rate of 1 mL min^{-1} [26]. Other degradation prod-