



Nanostructured δ -FeOOH: An efficient Fenton-like catalyst for the oxidation of organics in water

Izabela S.X. Pinto^a, Pedro H.V.V. Pacheco^a, Jakelyne Viana Coelho^b, Eudes Lorençon^b, José D. Ardisson^c, José D. Fabris^d, Patterson P. de Souza^e, Klaus W.H. Krambrock^f, Luiz C.A. Oliveira^{b,*}, Márcio C. Pereira^a

^a Instituto de Ciência, Engenharia e Tecnologia, Universidade Federal dos Vales do Jequitinhonha e Mucuri, 39803-371 Teófilo Otoni, Minas Gerais, Brazil

^b Departamento de Química, ICEX, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, Minas Gerais, Brazil

^c Centro de Desenvolvimento da Tecnologia Nuclear, 31270-901 Belo Horizonte, Minas Gerais, Brazil

^d Universidade Federal dos Vales do Jequitinhonha e Mucuri, 39100-000 Diamantina, Minas Gerais, Brazil

^e Departamento de Química, Centro Federal de Educação Tecnológica de Minas Gerais, 30480-000 Belo Horizonte, Minas Gerais, Brazil

^f Departamento de Física, ICEX, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, Minas Gerais, Brazil

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ABSTRACT

δ -FeOOH nanoparticles were prepared by the precipitation of $\text{Fe}(\text{OH})_2$ followed by rapid oxidation with H_2O_2 . Samples with different surface areas and particle sizes were obtained by controlling the final pH of the reaction medium. The samples were characterized by X-ray powder diffractometry, ^{57}Fe Mössbauer spectroscopy, saturation magnetization measurements, total Fe chemical analyses and BET surface area measurements. The catalytic activities of these samples for H_2O_2 decomposition were strongly influenced by the δ -FeOOH surface area. EPR was used to monitor catalytic H_2O_2 decomposition in the presence of methanol, indicating that the mechanism of decomposition involves radicals in accord with the Haber–Weiss mechanism. Methylene blue and indigo carmine were used to simulate the degradation of contaminants. Monitoring these experiments with ESI-MS revealed that δ -FeOOH can activate H_2O_2 to produce reactive radicals, which can further promote the oxidation of the dyes. The dye degradation rates depended on the amount of Fe^{2+} generated *in situ* on the δ -FeOOH surface.

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1. Introduction

In the last decade, several systems based on Fe-bearing solids, such as iron oxides [1–11], zeolites [12], pillared clays [13], and alumina [14], have been investigated for use in environmental remediation processes. Iron oxides are good candidates for use as heterogeneous Fenton-like catalyst because they are reactive at neutral pH. This avoids the need for the acidification and neutralization steps used in the homogeneous Fenton process and thereby avoids sludge formation. The heterogeneous catalysts can also be easily recycled, and all operations in the effluent treatment are significantly simplified if the solid catalyst is easy to handle.

Among the iron oxides, magnetite (ideal formula Fe_3O_4) has been widely reported as a suitable Fenton-like catalysis because of its magnetic and redox properties, which are strongly affected by the isomorphous substitution of Fe by other cations. For instance, the isomorphous substitution of Fe^{2+} by Co^{2+} or Mn^{2+} causes a significant increase in the reactivity of the system, whereas Ni^{2+} doping retards

the catalytic activity of magnetite to activate the H_2O_2 molecule [3]. However, the main problem in the use of magnetite as a Fenton-like catalyst lies in is the atmospheric oxidation of structural Fe^{2+} to Fe^{3+} . This oxidation produces an outer Fe^{3+} oxide layer which passivates the magnetite surface and inhibits the catalytic efficiency toward Fenton-like catalysis.

Lee et al. [15] compared the catalytic efficiency of homogeneous Fenton and commercial goethite, hematite and magnetite to oxidize phenol in the presence of H_2O_2 . The efficiency of the catalysts decreased in the sequence $\text{Fe}^{2+} \gg \text{magnetite} \approx \text{hematite} > \text{goethite}$. Composites based on goethite supported on a silica matrix to degrade phenol in the presence of H_2O_2 and oxalic acid. However, the reactivity of this system to oxidize phenol was correlated with dissolutive capacity of Fe by oxalic acid, and therefore homogeneous Fenton take place [16].

The use of iron oxides such as magnetite (Fe_3O_4) [1–3], hematite (α - Fe_2O_3) [4,5], maghemite (γ - Fe_2O_3) [6,7] and goethite (α -FeOOH) [6–9] as heterogeneous Fenton-like catalysts is very well documented in the literature. However, to the best of our knowledge, only one study [17] has reported the use of δ -FeOOH as a Fenton-like catalyst. No studies on the effects of the physical and chemical properties of δ -FeOOH on the catalytic properties have been reported.

* Corresponding author. Tel.: +55 31 3409 6384; fax: +55 31 34095700.

E-mail address: luizoliveira@qui.ufmg.br (L.C.A. Oliveira).

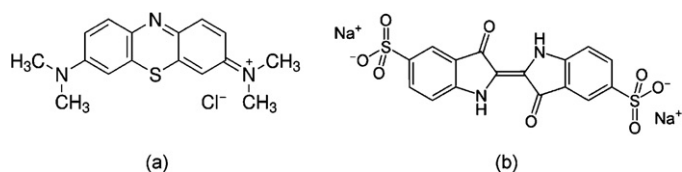


Fig. 1. Molecular structure of (a) methylene blue and (b) indigo carmine.

δ -FeOOH is a polymorph of four known iron oxyhydroxides, with a structure that is based on a hexagonal closed-packed oxygen lattice similar to that of hematite (α -Fe₂O₃) [18], where iron occupies half of the available octahedral interstices [19]. It presents some advantages for use in heterogeneous catalysis because (i) nanoparticles can be easily synthesized; (ii) the high surface area results in more contact between the catalyst, the H₂O₂ and the contaminant, thus increasing the efficiency of H₂O₂ activation and thereby the oxidation of organic compounds; (iii) it is ferrimagnetic at room temperature, thus the catalyst can be easily recovered after the reaction using a simple magnet and (iv) its synthesis is cheap due to the ample availability of the raw material, as iron is one of the most abundant elements on Earth.

Thus, the objective of the present study was to investigate the influence of the chemical and physical properties of δ -FeOOH nanoparticles on H₂O₂ decomposition and dye oxidation. δ -FeOOH materials with different particle sizes and surface areas were synthesized by the precipitation of Fe(OH)₂ followed by rapid oxidation with H₂O₂. The material's viability as a heterogeneous catalyst was tested by its ability to degrade a cationic dye (methylene blue) (Fig. 1a) and an anionic dye (indigo carmine) (Fig. 1b) in aqueous media.

2. Experimental methods

2.1. Synthesis of δ -FeOOH

The synthesis of δ -FeOOH was carried out using analytically pure chemicals and doubly distilled water. Because of strong foaming in the course of Fe²⁺ oxidation with H₂O₂, the sample was prepared in a specially designed glass reactor. In short, 200 mL of a solution containing 5.5604 g of FeSO₄(NH₄)₂SO₄·6H₂O was mixed with 200 mL of a 2 M NaOH solution. A green precipitate (green rust) was formed. Immediately, 5 mL of 30% H₂O₂ was added with stirring. The precipitate turned reddish brown within a few seconds, indicating the formation of δ -FeOOH. δ -FeOOH samples with different particle sizes and surface areas were obtained by changing the final pH of the suspension by adding concentrated HCl or NaOH solutions and monitoring the pH with test strips. The precipitate was washed with distilled water several times and dried in a vacuum desiccator at room temperature. The samples were labeled according to the final pH of the suspension, i.e., F12, F12.5, F13.5 and F14.

2.2. Characterization

The total Fe content of the δ -FeOOH samples was determined by volumetric titration with a K₂Cr₂O₇ solution. Saturation magnetization measurements were performed using a portable magnetometer [20]. Surface areas were determined by the BET method using a 22 point N₂ adsorption/desorption procedure in an Autosorb 1 Quantachrome gas sorption analyzer.

X-ray diffraction (XRD) was carried out using Cu-K α radiation with a Rigaku Geigerflex diffractometer equipped with a graphite diffracted-beam monochromator. Data were collected from 20° to 70° 2 θ in steps of 0.02° per 5-s iteration.

Mössbauer spectra were collected in constant acceleration transmission mode with a 10 mCi ⁵⁷Co/Rh source. The spectra of δ -FeOOH samples were taken at 298 K and at 20 K using a liquid helium bath cryostat. Doppler velocities ranged between ± 2 mm s⁻¹ at room temperature and ± 12 mm s⁻¹ at 20 K. The data were stored in a 1024-channel MCS memory unit and were fitted using the NORMOS program. Isomer shifts were calculated relative to α -Fe.

2.3. Catalytic tests

Hydrogen peroxide (2.8 M) decomposition was studied by measuring the formation of gaseous O₂ in a volumetric glass system at pH \approx 6.3 using 30 mg catalyst aliquots.

The oxidation of 0.04 g L⁻¹ methylene blue with H₂O₂ was carried out at pH 6 in the presence of 30 mg of catalyst and monitored by UV/vis spectroscopy at 663 nm, using a Varian Cary 5 spectrometer.

The oxidation of 0.05 g L⁻¹ indigo carmine with H₂O₂ was carried out at pH 6.5 in the presence of 30 mg of catalyst and monitored by UV/vis spectroscopy at 612 nm using a Varian Cary 5 spectrometer. All reactions were performed at 26 \pm 1 °C in a recirculating temperature-controlled bath. The Fe concentrations in the solutions after the reactions were determined by atomic absorption spectrometry using a Varian SpectrAA210 spectrometer.

2.4. Electrospray ionization (ESI)-mass spectrometry (MS)

To identify the intermediate chemical species of the methylene blue oxidation reaction, an ION-TRAP LCQ Fleet (ThermoScientific, San Jose, CA) was used in positive ion mode. The reaction samples were analyzed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 15 L min⁻¹. Spectra were obtained as averages of 5 scans of 0.2 s each. Typical ESI conditions used a heated capillary temperature of 275 °C, sheath gas (N₂) at a flow rate of 15 units (ca. 4 L min⁻¹), a spray voltage of 2 kV, a capillary voltage of 25 V and a tube lens offset voltage of 25 V.

2.5. EPR study

To investigate the possibility of the formation of radical species in our system, an EPR study was performed. In a typical experiment, 10 mg of a δ -FeOOH sample were dispersed into 10 mL of a 2 wt.% poly(vinyl alcohol) aqueous solution. The reaction was initiated by the addition of 10 mL of cyclohexane containing 10 mM of PBN (N-t-Butyl- α -phenylnitron) and 0.1 mL of hydrogen peroxide (30% v/v) to the emulsion with vigorous stirring. Then, 100 μ L aliquots from the cyclohexane organic phase (the upper layer) were quickly transferred to a precision bore quartz EPR tube with a diameter of 3 mm. The (EPR) spectra were recorded at room temperature with a custom-built X-band spectrometer (9.38 GHz) using a commercial cylindrical cavity (Bruker), a klystron (Varian) and an electromagnet (Varian) with a maximum field amplitude of 800 mT. For the g factor calibration, 1,1-diphenyl-2-picrylhydrazyl (DPPH) was used as the standard ($g = 2.0037$).

3. Results and discussion

3.1. Characterization of the δ -FeOOH samples

The δ -FeOOH samples were prepared by the precipitation of Fe(OH)₂ followed by rapid oxidation with H₂O₂. The XRD patterns of samples F14, F13.5 and F12.5 (Fig. 2) showed a single phase corresponding to δ -FeOOH, which was identified by 1 0 0, 1 0 1, 1 0 2 and 1 1 0 diffraction maxima consistent with those of JCPDS File

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