



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Improved photocatalytic activity of δ -FeOOH by using H_2O_2 as an electron acceptor



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ARTICLE INFO

Article history:

Received 9 April 2016

Received in revised form 11 July 2016

Accepted 8 August 2016

Available online 9 August 2016

Keywords:

Iron oxides
Photocatalysts
Photodegradation
Dye oxidation
Fenton

ABSTRACT

In this work, δ -FeOOH nanoparticles were synthesized by a simple co-precipitation method and used as a photocatalyst in the presence of H_2O_2 for the oxidation of Rhodamine B (RhB) dye under artificial light. The δ -FeOOH was characterized by powder X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, N_2 adsorption/desorption and UV–vis diffuse reflectance measurements. The δ -FeOOH nanoparticles have high specific surface area ($101\text{ m}^2\text{ g}^{-1}$) and optical bandgap energy of 2.02 eV. Under artificial light, only 59% of RhB (100 mL ; 20 mg L^{-1}) was photocatalytically degraded by δ -FeOOH in 60 min reaction. However, after adding H_2O_2 , the photocatalytic activity of δ -FeOOH was significantly improved, reaching 87% of dye removal. Tests using scavengers of reactive species and EPR analysis revealed that h^+ and $\cdot\text{OH}$ are the main species in this system. Based on the experimental results, the mechanism of RhB photodegradation in the presence of δ -FeOOH and H_2O_2 was proposed. By this mechanism, the $\cdot\text{OH}$ can be formed by direct water oxidation or by H_2O_2 reduction, as the electron transfer from the conduction band of δ -FeOOH to H_2O_2 is thermodynamically favorable. Moreover, the H_2O_2 retards the electron-hole recombination in δ -FeOOH, thus increasing its photocatalytic activity. Given its high efficiency for degrading RhB in water, δ -FeOOH revealed to be a promising photocatalyst to be tested in the oxidation of emerging pollutants for the environmental decontamination.

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1. Introduction

The effluents from textile industries are increasingly becoming an environmental problem because of the toxicity of the dyes used in the dyeing process [1]. Conventional wastewater treatment technologies have proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants [2]. Therefore, several advanced oxidation processes (AOPs), including ozonation, Fenton, photo-Fenton, and photocatalytic oxidation, have been proposed as interesting alternatives to other more conventional treatments [3–11]. Among these AOPs, the photocatalysis has attracted considerable attention due to its effectiveness for degrading pollutants under light irradiation [12].

Photocatalysis involves the activation of a semiconductor material by light. A semiconductor is characterized by its bandgap energy, which is the difference between the energies of the valence and conduction bands. The absorption of photons by a semiconductor with energy higher than its bandgap energy promotes the excitation of electrons (e^-) from the valence band to the conduction band, thus generating an electronic hole (h^+) in the valence band of the semiconductor. These photogenerated electrons and holes can then react with the substrates on the photocatalyst surface for producing reduced and oxidized species, respectively [13,14].

Iron-based materials have been reported to be promising for the photocatalytic oxidation of organic contaminants in wastewater due to its high ability to generate hydroxyl radicals ($\cdot\text{OH}$), which are strongly oxidant and non-selective species [15]. Recently, Lima et al. [16] reported the use of δ -FeOOH nanoparticles as a photocatalyst for the oxidation of dyes in water. However, the single δ -FeOOH exhibited too low photocatalytic activity under

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UVA light, probably because of the fast bulk and surface e^-/h^+ recombination. To solve this drawback, an attractive strategy to decrease or eliminate the surface recombination consists in using a redox couple with more negative reduction potential than that of water. The reduction potential of the $\cdot\text{OH}/\text{H}_2\text{O}_2$ couple ($E^\ominus = +0.87\text{ V vs. NHE}$) [17] is more negative than that of the $\cdot\text{OH}/\text{H}_2\text{O}$ couple ($E^\ominus = +2.80\text{ V vs. NHE}$), meaning that the H_2O_2 molecule may be more readily oxidized than water. Thus, if the energy level of the valence band of a semiconductor is more positive than the reduction potential of H_2O_2 , the holes in the valence band of the semiconductor could oxidize H_2O_2 to produce superoxide radicals $\text{O}_2^{\cdot-}$ as follows (Eq. (1)) [18]:



On the other hand, if the energy level of the conduction band of a semiconductor is more negative than the reduction potential of H_2O_2 , it could reduce the H_2O_2 to form $\cdot\text{OH}$ radicals (Eq. (2)) [19]:



With this in mind, we report in this work a simple strategy to minimize the fast electron-hole recombination in $\delta\text{-FeOOH}$ nanoparticles by using H_2O_2 as an electron acceptor in order to enhance the photocatalytic activity of $\delta\text{-FeOOH}$ for the degradation of Rhodamine B (RhB) dye in water.

2. Materials and methods

2.1. Material preparation

The synthesis of $\delta\text{-FeOOH}$ was carried out as described elsewhere with some modifications [20–22]. Briefly, the $\delta\text{-FeOOH}$ nanoparticles were prepared by mixing 100 mL of a 2 M NaOH solution with 100 mL of a solution containing 5.5604 g of $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$. After the formation of a green rust precipitated, 5 mL of 30% H_2O_2 was immediately added with stirring. The precipitate turned reddish brown within a few seconds, indicating the formation of $\delta\text{-FeOOH}$ nanoparticles. The precipitate was washed with distilled water several times and dried in a vacuum desiccator at room temperature.

2.2. Characterization

Powder XRD data were obtained with an RIGAKU GEIGERFLEX diffractometer equipped with a graphite diffracted beam monochromator. Data were collected in a 2θ range of $20\text{--}80^\circ$ using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.541838\text{ \AA}$) and a scanning speed of 2° min^{-1} . Silicon was used as an external standard. ^{57}Fe Mössbauer spectrum was collected using a CMTE spectrometer model MA250 in constant acceleration transmission mode with a 5 mCi $^{57}\text{Co}/\text{Rh}$ gamma-ray source at room temperature. The data were stored in 1024 channels and fitted using the WinNormosTM for Igor. Isomer shift values were quoted relatively to the $\alpha\text{-Fe}$ foil. The UV-vis diffuse reflectance spectrum was taken on dry, ground powders using a Varian Cary 5 spectrophotometer equipped with a diffuse reflectance accessory. BaSO_4 powder was used as a reference (100% transmission). Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics ASAP-2000 instrument, and the specific surface area was calculated using the BET model.

2.3. Reactions

The Fenton-like oxidation of RhB (20 mg L^{-1}) with 0.30 mL of H_2O_2 (30% v/v) at pH 6.0 was carried out with the dye in the total volume of 100 mL and 100 mg of $\delta\text{-FeOOH}$ catalyst. The photocatalytic activity of $\delta\text{-FeOOH}$ (100 mL of 20 mg L^{-1} RhB + 100 mg

catalyst + light) was tested in a cylindrical batch photoreactor. A high-pressure mercury lamp (HPK 125 W, Philips) with a water-cooled filter served as a light source. The HPK lamp provides maximum energy at 365 nm, with substantial radiation also at 435, 313, 253 and 404 nm. The intensity of the light reaching the reactor was measured with a pyranometer separate sensor with a handheld meter (APG-MP-200) and estimated to be 14 mW cm^{-2} . The catalytic activity of $\delta\text{-FeOOH}$ in a combined system (photocatalysis + H_2O_2) was performed at the same conditions of photocatalysis, except by the addition of 0.3 mL of H_2O_2 (30% v/v). All the reactions were monitored by UV-vis measurements after the separation of the catalyst nanoparticles from the RhB aliquot by centrifugation at 4000 rpm for 5 min. The reactions were carried out in duplicates under a magnetic stirring in a recirculating temperature controlled bath kept at $25 \pm 1^\circ\text{C}$.

The evaluation of the reactive species generated during the photooxidation of RhB in the presence of H_2O_2 was based on the use of different scavenger molecules (benzoquinone, isopropanol, and ammonium oxalate to trap $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$ and h^+ , respectively), which were introduced into the reaction medium before the addition of $\delta\text{-FeOOH}$. The dosage of these scavengers was 10 mM.

Hydroxyl radicals were determined by a DMPO spin-trapping EPR method at room temperature on a Bruker ER200-D-SRC spectrometer at X-band, equipped with a high-pressure mercury lamp (125 W). Experiments were performed with a capillary Pyrex glass tube under fixed conditions (100 mg catalyst, 0.3 mL H_2O_2 (30% v/v), and 200 mM DMPO), and the EPR spectra were recorded after 60 min of light irradiation.

The Mott-Schottky measurement was carried out with an AUTOLAB Potentiostat-Galvanostat PGSTAT 128N using a standard three-electrode cell with an Ag/AgCl (3.0 M KCl) reference electrode, a platinum wire as a counter electrode and $\delta\text{-FeOOH}$ as a working electrode with irradiation area of 0.5 cm^2 . A 0.5 M Na_2SO_4 aqueous solution was used as an electrolyte, and the frequency was in the range of 1–100 mHz.

3. Results and discussion

3.1. Materials characterization

The X-ray diffraction pattern of $\delta\text{-FeOOH}$ is shown in Fig. 1. It was identified by its (100), (002), (102), (110), and (200) (hkl) planes, according to the JCPDS File 13-87. The XRD pattern was indexed on a hexagonal cell with parameters $a = 2.940(3)\text{ \AA}$ and $c = 4.563(2)\text{ \AA}$. The average crystallite size was estimated by the Scherrer equation as being $14 \pm 2\text{ nm}$.

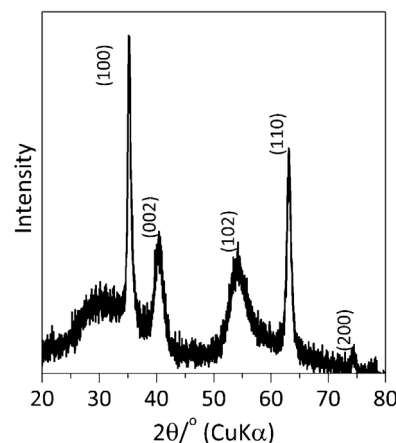


Fig. 1. Powder X-ray diffraction pattern of $\delta\text{-FeOOH}$ sample.

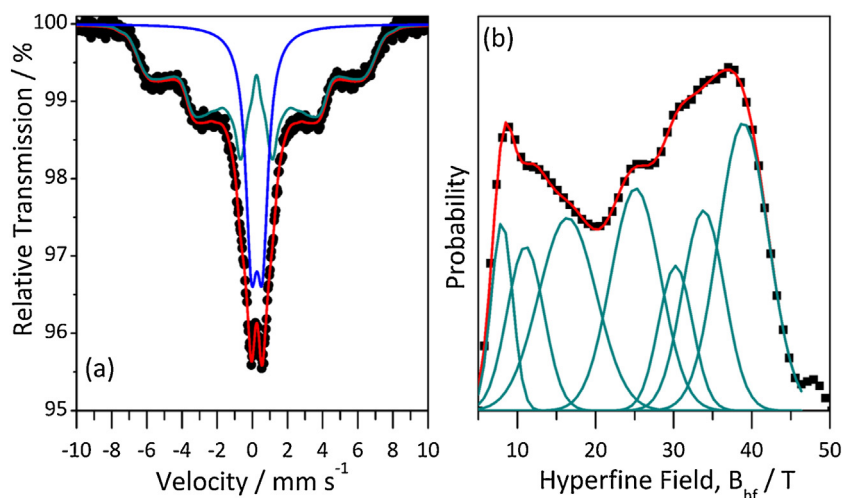


Fig. 2. (a) 298 K Mössbauer spectrum of δ -FeOOH nanoparticles and (b) hyperfine field distribution for the Fe^{3+} in the δ -FeOOH.

The Mössbauer spectrum at 298 K was fitted with a distribution of magnetic hyperfine field (broad sextet, Fig. 2a and b) due to the particle size distribution and a doublet (blue line; $\delta = 0.38 \text{ mm s}^{-1}$ and $\Delta = 0.76 \text{ mm s}^{-1}$; Fig. 2a), which corresponds to smaller δ -FeOOH particles. The maximum hyperfine field was 39.1 T (Fig. 2a), and the quadrupole shift was $-0.10(2) \text{ mm s}^{-1}$. The isomer shift of $0.38(1) \text{ mm s}^{-1}$ confirms that the Fe^{3+} ions are located on octahedral sites in the δ -FeOOH structure.

The UV–vis spectrum of δ -FeOOH (Fig. 3a) revealed that it absorbs light over a broad range of the UV and visible light spectra, which may allow it to absorb a substantial amount of solar light. The optical indirect band gap energy of δ -FeOOH was calculated using Eq. (3) [23]:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (3)$$

where α = absorption coefficient, h = Planck's constant, ν = light frequency, A = proportionality constant and E_g = optical band gap energy. Thus, the optical band gap energy of δ -FeOOH was determined as being 2.02 eV (Fig. 3b).

The N_2 adsorption-desorption curve of δ -FeOOH is shown in Fig. 4a, and the corresponding pore size distribution is presented in Fig. 4b. The N_2 adsorption-desorption curve exhibited a type IV isotherm, which is characteristic of mesoporous materials (Fig. 4b), with a type H3 hysteresis loop. The BET specific surface area was

$101 \text{ m}^2 \text{ g}^{-1}$ and the pore diameter of δ -FeOOH was in the range of 20–440 Å with a maximum probability centered at 24 Å.

3.2. Photocatalytic activity

The catalytic activity of δ -FeOOH was evaluated through H_2O_2 reaction in the dark (Fenton-like reaction), photocatalysis under artificial light, and photocatalysis + H_2O_2 combined process (Fig. 5). RhB was used as a model of dye contaminant. Control experiments based on dye adsorption in the dark, RhB + H_2O_2 in the dark, RhB photolysis and RhB photolysis + H_2O_2 were performed because these process may also contribute to the discoloration of the RhB dye. At pH 6.6, the RhB adsorption by δ -FeOOH in the absence of light and H_2O_2 was only 13% after 60 min (Fig. 5). After the adsorption equilibrium had been achieved (24 h adsorption under stirring in the dark), only 16% of the RhB was removed from the solution, indicating that the most of the adsorption takes place at the first adsorption hour. The low RhB adsorption capacity of δ -FeOOH can be assigned to electrostatic repulsion between the positively charged surface of δ -FeOOH ($\text{pH}_{\text{pzc}} = 8.4$) [24] and the cationic dye at pH 6.6. In the presence of H_2O_2 in the dark (heterogeneous Fenton-like reaction), approximately 11% of the RhB color was removed after 60 min reaction (Fig. 5), suggesting that in the dark the δ -FeOOH was inactive towards H_2O_2 reaction.

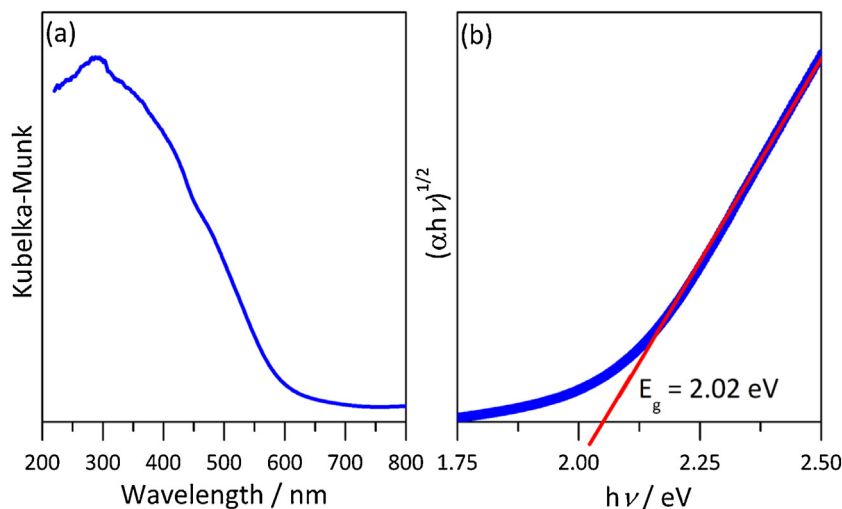


Fig. 3. (a) UV–vis diffuse reflectance spectra of δ -FeOOH nanoparticles. (b) Tauc's plot for the bandgap calculation.

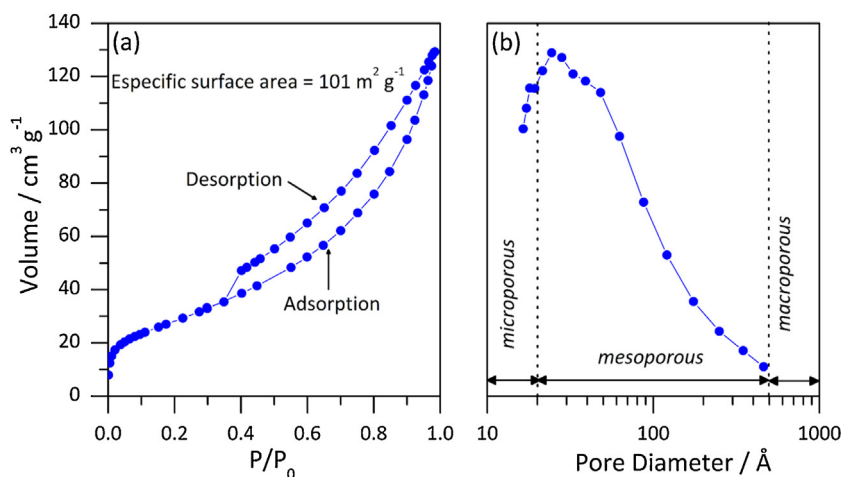


Fig. 4. (a) Nitrogen adsorption–desorption isotherm and (b) pore size distribution for the δ -FeOOH nanoparticles.

Pinto et al. [25] reported that the δ -FeOOH can react with H_2O_2 to produce $\cdot\text{OH}$, which can further attack the organic molecules to form oxidized products. However, because the δ -FeOOH is constituted only by Fe^{3+} ions (according to Mössbauer measurements), the kinetics of H_2O_2 activation is too slow, and therefore, the color removal by the Fenton-like reaction in the presence of δ -FeOOH was negligible. The single H_2O_2 (in the dark) and the photolysis (only light+dye) did not generate RhB oxidized products (Fig. 5). On the other hand, in the presence of light and H_2O_2 , 64% of the total color of RhB was removed, indicating that the light has a significant role in forming reactive species from H_2O_2 . The RhB color removal due to the photocatalysis (δ -FeOOH + light) was 59% after 60 min reaction. However, it is known that the photocatalytic activity of δ -FeOOH is limited by the fast electron-hole recombination in that photocatalyst [16]. To minimize these effects, H_2O_2 was used as an electron trap to improve the photocatalytic activity of δ -FeOOH. Consequently, the photocatalysis in the presence of H_2O_2 removed 87% of RhB after 60 min reaction. The higher photocatalytic activity exhibited by the δ -FeOOH in the presence of H_2O_2 may be due to the combined effects of H_2O_2 +light to form reactive species (e.g. $\cdot\text{OH}$) and improved photocatalysis due to the minimizing of the photo-generated electron-hole recombination by using H_2O_2 as an electron acceptor.

Under visible-light irradiation (White LED $\lambda > 450$ nm, 5 mW cm^{-2}) the RhB degradation was very slow as compared to that

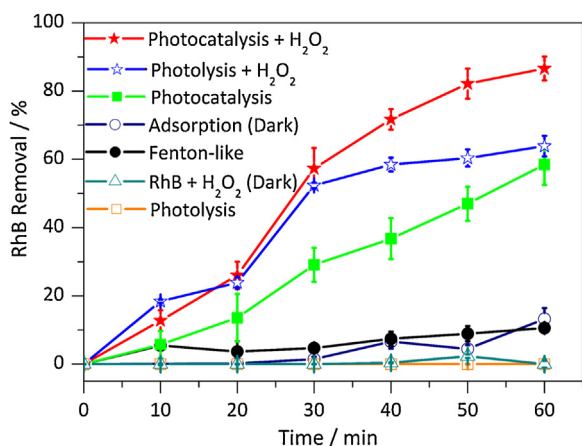


Fig. 5. Kinetics of RhB degradation by different processes in the presence of δ -FeOOH.

Table 1

Rate constants of RhB discoloration on δ -FeOOH under UV and visible light irradiation at initial pH 6.6.

Sample	k_{UV} (min^{-1})	k_{vis} (10^{-3} min^{-1})
Photocatalysis	0.018	0.011
Photolysis + H_2O_2	0.023	0.002
Photocatalysis + H_2O_2	0.043	0.019

k_{UV} and k_{vis} are the constants measured under UV (high-pressure mercury lamp) and visible light irradiation, respectively.

under UV irradiation (Table 1). This indicates that light-induced RhB degradation mainly occurs through the ligand-to-metal charge transfer transition ($\text{O}^{2-} \rightarrow \text{Fe}^{3+}$) whereas the $d-d$ excited states of δ -FeOOH ($\text{Fe}^{3+} \rightarrow \text{Fe}^{3+}$) are not important for photocatalytic degradation of dyes. A similar photocatalytic behavior for various iron oxyhydroxides has been reported elsewhere [26].

3.3. Study of the reactive species

The reactive species in the oxidation of RhB in the presence of δ -FeOOH and H_2O_2 were monitored by employing different scavengers, since the photocatalytic oxidation of RhB in the presence of H_2O_2 may occur via different reactive species such as h^+ , $\cdot\text{OH}$ and/or $\text{O}_2^{\cdot-}$. It is very well known that ammonium oxalate, isopropanol and benzoquinone can trap the h^+ , $\cdot\text{OH}$, and $\text{O}_2^{\cdot-}$ species, respectively [27]. Thus, by adding scavengers before the RhB photodegradation reaction, the corresponding reactive species can be evaluated based on changes in the photocatalytic activity of δ -FeOOH.

Fig. 6 shows the photocatalytic activity of δ -FeOOH in the oxidation of RhB under different conditions. In the absence of scavengers, the removal of RhB was 87% after 60 min reaction. By adding benzoquinone to suppress $\text{O}_2^{\cdot-}$, the oxidation efficiency of RhB was not affected, indicating that the $\text{O}_2^{\cdot-}$ is not a significant reactive species in this reaction. On the other hand, when ammonium oxalate was used as a hole trap, the photodegradation of RhB decreased to 60%, suggesting that the photogenerated holes are crucial to the photodegradation process using δ -FeOOH as a catalyst. In the presence of isopropanol, the photodegradation efficiency was significantly decreased to 48%. Based on these results, it is evident that $\cdot\text{OH}$ and h^+ are the main reactive species in the photocatalytic reaction mediated by δ -FeOOH in the presence of H_2O_2 .

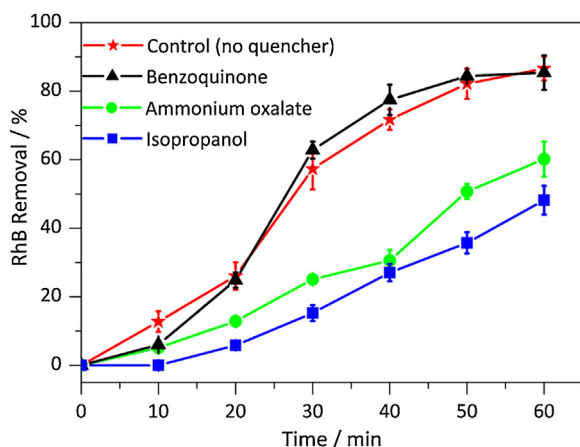


Fig. 6. Kinetics of photodegradation of RhB in the presence of δ -FeOOH, H_2O_2 , and different scavengers. [RhB] = 20 mg L^{-1} , RhB volume = 100 mL, catalyst mass = 100 mg, H_2O_2 (30%v/v) volume = 0.3 mL, scavenger dosage = 10 mM, and light source = high-pressure mercury lamp (14 mW cm^{-2}).

In general, $\cdot\text{OH}$ can result from the H_2O_2 reduction (Eq. (2)), H_2O_2 photolysis, and/or from water oxidation (Eq. (4)) [28]:



To verify the main source for $\cdot\text{OH}$ production, the reactions in the presence of light were examined by a DMPO spin-trapping EPR technique (Fig. 7). In the presence of δ -FeOOH and light, small signals of DMPO – $\cdot\text{OH}$ adducts were observed, indicating that $\cdot\text{OH}$ can be produced by water oxidation according to Eq. (4). The signals of DMPO – $\cdot\text{OH}$ adducts for $\text{H}_2\text{O}_2 + \text{light}$ suggest that direct photolysis of H_2O_2 into $\cdot\text{OH}$ has also occurred. Interestingly, the signal intensity for the δ -FeOOH + $\text{H}_2\text{O}_2 + \text{light}$ was significantly higher than that of H_2O_2 photolysis and water oxidation, thus supporting our hypothesis that H_2O_2 can accept electrons from the conduction band of δ -FeOOH to produce $\cdot\text{OH}$.

3.4. Proposed RhB photodegradation mechanism

To understand the origin of the highest photocatalytic activity exhibited by δ -FeOOH in the presence of H_2O_2 , it is useful to determine the potential energy diagram of δ -FeOOH. To determine the relative band position of δ -FeOOH, we first measured its flatband potential according to the Mott-Schottky equation

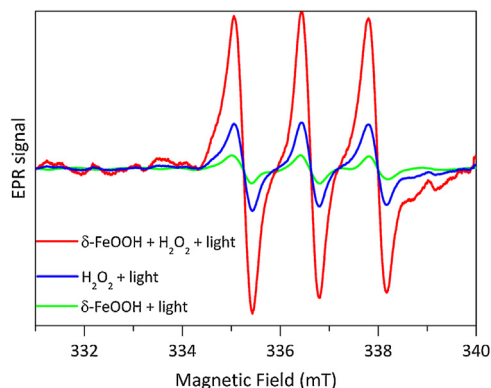


Fig. 7. EPR spectra of DMPO – $\cdot\text{OH}$ adducts recorded with δ -FeOOH under a high-pressure mercury lamp in the presence and the absence of H_2O_2 .

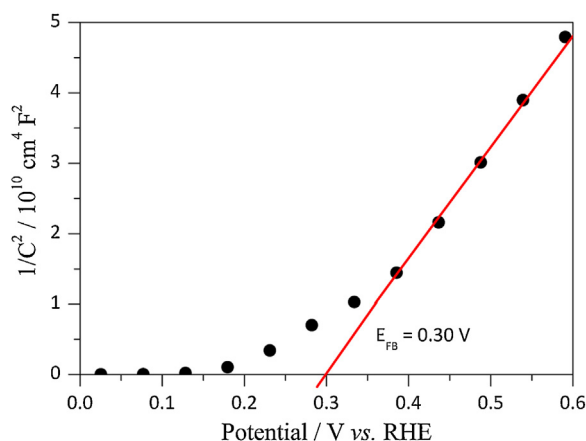


Fig. 8. Mott-Schottky plot of δ -FeOOH measured in 0.5 M Na_2SO_4 (pH = 6.6) at 10 Hz.

(Eq. (5)) [29].

$$\frac{1}{C^2} = \left(\frac{2}{e\epsilon\epsilon_0 N_D} \right) \left(E - E_{\text{FB}} - \frac{kT}{e} \right) \quad (5)$$

where C is the space charge capacitance (F cm^{-2}), e is the electron charge (C), ϵ is the dielectric constant of the semiconductor, ϵ_0 is the permittivity of free space, N_D is the carrier density (cm^{-3}), E is the applied potential (V), E_{FB} is the flatband potential (V), k is the Boltzmann constant, and T represents the temperature in K. Thus, the flatband potential can be obtained from the x-intercept of the tangent line of the Mott-Schottky plot versus the potential axis. From Fig. 8, it can be noted that the δ -FeOOH synthesized in this work exhibited an n-type behavior, as verified by the positive slope of the Mott-Schottky plot. The flatband potential of δ -FeOOH at pH 6.6 was determined as being about 0.30 V vs. NHE (Fig. 8). Assuming the gap between the flatband potential and the bottom edge of the conduction band is negligible for n-type semiconductors, that flatband potential value reflects the conduction band level of δ -FeOOH at pH 6.6.

Based on the determined values of flatband potential and optical bandgap energies, we estimated the valence band energy ($E_{\text{VB}} = E_{\text{g}} + E_{\text{CB}}$) and built the potential energy diagram for the δ -FeOOH (Fig. 9). Thus, according to the proposed mechanism of RhB photooxidation, first the δ -FeOOH absorbs radiation with energy superior to 2.02 eV to promote electrons from the valence band to the conduction band of δ -FeOOH. Consequently, electronic holes are produced in the valence band of the photocatalyst. Once these charges are generated and separated, they can react with

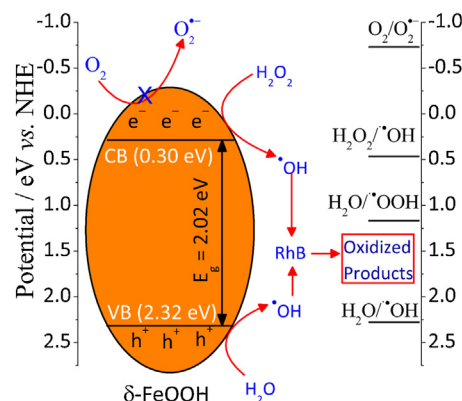


Fig. 9. Schematic energy diagram for the δ -FeOOH and the proposed mechanism of the RhB photodegradation.

water, RhB, H₂O₂ or O₂. Our experimental data showed that the RhB was not degraded by the artificial light and, therefore, the direct electron transfer from the dye to the δ-FeOOH may not be the primary mechanism of RhB oxidation. Moreover, based on the energy diagram of δ-FeOOH, the electron transfer from the conduction band of δ-FeOOH to O₂ to form superoxide radical is thermodynamically unfavorable. In fact, the experiments using a scavenger for superoxide radical showed that the kinetics of RhB photodegradation was not affected, which suggests that O₂^{•-} is not important to the dye oxidation. On the other hand, tests with ammonium oxalate and isopropanol and EPR data revealed that the mechanism of RhB photodegradation takes place via h⁺ and •OH. Therefore, we propose that the h⁺ in the valence band of δ-FeOOH may oxidize water to produce the reactive •OH, whereas the electrons in the conduction band of δ-FeOOH can be transferred to H₂O₂ to form •OH. Hence, the photocatalytic activity of δ-FeOOH is improved by the addition of H₂O₂, which exerts two main roles: (i) to trap the electrons in the conduction band of δ-FeOOH, thus retarding the electron-hole recombination. Consequently, the h⁺ in the valence band can react with water to produce the •OH and (ii) to increase the number of hydroxyl radicals through the reduction of H₂O₂. Finally, the •OH can attack the RhB molecules to form colorless products.

4. Conclusions

In this work, we showed that the photocatalytic activity of δ-FeOOH under artificial light can be improved by using H₂O₂ as an electron trap. Because the energy level of the conduction band of δ-FeOOH is more negative than the reduction potential of H₂O₂, the transfer of electron from the conduction band of δ-FeOOH to the H₂O₂ was thermodynamically possible. The H₂O₂ takes place a fundamental role in the photocatalytic process by retarding the electron-hole recombination in δ-FeOOH, and increasing the formation of •OH. The h⁺ and •OH play a significant role in the RhB photodegradation. Finally, the photocatalytic system developed in this study is promising to be tested in the photodegradation of emerging contaminants, which are difficult to degrade by conventional methods.

Acknowledgements

The authors are grateful to PROPP/UFOP, FAPEMIG, CNPq and CAPES (Brazil) for the financial support. This work is a collaboration research project of members of the Rede Mineira de Química (RQ-MG) supported by FAPEMIG (Project: CEX - RED-00010-14).

References

- [1] P.V. Nidheesh, R. Gandhimathi, S.T. Ramesh, Degradation of dyes from aqueous solution by Fenton processes: a review, *Environ. Sci. Pollut. Res.* 20 (2013) 2099–2132.
- [2] E. Forgacs, T. Cserhati, G. Oros, Removal of synthetic dyes from wastewaters: a review, *Environ. Int.* 30 (2004) 953–971.
- [3] A. Bes-Piá, M.I. Iborra-Clar, A. Iborra-Clar, J.A. Mendoza-Roca, B. Cuartas-Urbe, M.I. Alcaina-Miranda, Nanofiltration of textile industry wastewater using a physicochemical process as a pre-treatment, *Desalination* 178 (2005) 343–349.
- [4] L.C.A. Oliveira, T.C. Ramalho, E.F. Souza, M. Goncalves, D.Q.L. Oliveira, M.C. Pereira, J.D. Fabris, Catalytic properties of goethite prepared in the presence of Nb on oxidation reactions in water: computational and experimental studies, *Appl. Catal. B-Environ.* 83 (2008) 169–176.
- [5] Q.Q. Chen, P.X. Wu, Y.Y. Li, N.W. Zhu, Z. Dang, Heterogeneous photo-Fenton photodegradation of reactive brilliant orange X-GN over iron-pillared montmorillonite under visible irradiation, *J. Hazard. Mater.* 168 (2009) 901–908.
- [6] A.C. Silva, D.Q.L. Oliveira, L.C.A. Oliveira, A.S. Anastacio, T.C. Ramalho, J.H. Lopes, H.W.P. Carvalho, C.E.R. Torres, Nb-containing hematites Fe_{2-x}Nb_xO₃: the role of Nb⁵⁺ on the reactivity in presence of the H₂O₂ or ultraviolet light, *Appl. Catal. A-Gen.* 357 (2009) 79–84.
- [7] M.C. Pereira, L.C.D. Cavalcante, F. Magalhaes, J.D. Fabris, J.W. Stucki, L.C.A. Oliveira, E. Murad, Composites prepared from natural iron oxides and sucrose: a highly reactive system for the oxidation of organic contaminants in water, *Chem. Eng. J.* 166 (2011) 962–969.
- [8] A.C. Silva, R.M. Cepera, M.C. Pereira, D.Q. Lima, J.D. Fabris, L.C.A. Oliveira, Heterogeneous catalyst based on peroxo-niobium complexes immobilized over iron oxide for organic oxidation in water, *Appl. Catal. B-Environ.* 107 (2011) 237–244.
- [9] M.C. Pereira, L.C.A. Oliveira, E. Murad, Iron oxide catalysts: Fenton and Fenton-like reactions—a review, *Clay Min.* 47 (2012) 285–302.
- [10] L.C.A. Oliveira, J.D. Fabris, M.C. Pereira, Iron oxides and their applications in catalytic processes: a review, *Quim. Nova* 36 (2013) 123–130.
- [11] M.A. Oaturan, Electrochemical advanced oxidation technologies for removal of organic pollutants from water, *Environ. Sci. Pollut. Res.* 21 (2014) 8333–8335.
- [12] D. Spasiano, R. Marotta, S. Malato, P. Fernandez-Ibanez, I. Di Somma, Solar photocatalysis: materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach, *Appl. Catal. B-Environ.* 170 (2015) 90–123.
- [13] X.J. Lang, X.D. Chen, J.C. Zhao, Heterogeneous visible light photocatalysis for selective organic transformations, *Chem. Soc. Rev.* 43 (2014) 473–486.
- [14] J.C. Colmenares, R. Luque, Heterogeneous photocatalytic nanomaterials: prospects and challenges in selective transformations of biomass-derived compounds, *Chem. Soc. Rev.* 43 (2014) 765–778.
- [15] C. Ruales-Lonfat, J.F. Barona, A. Sienkiewicz, M. Bensimon, J. Velez-Colmenares, N. Benitez, C. Pulgarin, Iron oxides semiconductors are efficient for solar water disinfection: a comparison with photo-Fenton processes at neutral pH, *Appl. Catal. B-Environ.* 166 (2015) 497–508.
- [16] L.V.C. Lima, M. Rodriguez, V.A.A. Freitas, T.E. Souza, A.E.H. Machado, A.O.T. Patrocínio, J.D. Fabris, L.C.A. Oliveira, M.C. Pereira, Synergism between n-type WO₃ and p-type delta-FeOOH semiconductors: high interfacial contacts and enhanced photocatalysis, *Appl. Catal. B-Environ.* 165 (2015) 579–588.
- [17] B.H.J. Bielski, D.E. Cabelli, R.L. Arudi, A.B. Ross, Reactivity of HO₂/O₂⁻ radicals in aqueous-solution, *J. Phys. Chem. Ref. Data* 14 (1985) 1041–1100.
- [18] T. Hirakawa, K. Yawata, Y. Nosaka, Photocatalytic reactivity for O₂^{•-} and OH radical formation in anatase and rutile TiO₂ suspension as the effect of H₂O₂ addition, *Appl. Catal. A-Gen.* 325 (2007) 105–111.
- [19] V.K. Gupta, R. Jain, A. Mittal, M. Mathur, S. Sikarwar, Photochemical degradation of the hazardous dye Safranin-T using TiO₂ catalyst, *J. Colloid Interface Sci.* 309 (2007) 464–469.
- [20] M.C. Pereira, E.M. Garcia, A.C. da Silva, E. Lorencon, J.D. Ardisson, E. Murad, J.D. Fabris, T. Matencio, T.D. Ramalho, M.V.J. Rocha, Nanostructured δ-FeOOH: a novel photocatalyst for water splitting, *J. Mater. Chem.* 21 (2011) 10280–10282.
- [21] T.D. Rocha, E.S. Nascimento, A.C. da Silva, H.D. Oliveira, E.M. Garcia, L.C.A. de Oliveira, D.S. Monteiro, M. Rodriguez, M.C. Pereira, Enhanced photocatalytic hydrogen generation from water by Ni(OH)₂ loaded on Ni-doped δ-FeOOH nanoparticles obtained by one-step synthesis, *RSC Adv.* 3 (2013) 20308–20314.
- [22] P. Chagas, A.C. da Silva, E.C. Passamani, J.D. Ardisson, L.C.A. de Oliveira, J.D. Fabris, R.M. Paniago, D.S. Monteiro, M.C. Pereira, δ-FeOOH: a superparamagnetic material for controlled heat release under AC magnetic field, *J. Nanopart. Res.* 15 (2013) 1–7.
- [23] J.J. Tauc, *Amorphous and Liquid Semiconductors*, Plenum, London, 1974.
- [24] M.C.S. Faria, R.S. Rosemberg, C.A. Bomfeti, D.S. Monteiro, F. Barbosa, L.C.A. Oliveira, M. Rodriguez, M.C. Pereira, J.L. Rodrigues, Arsenic removal from contaminated water by ultrafine δ-FeOOH adsorbents, *Chem. Eng. J.* 237 (2014) 47–54.
- [25] I.S.X. Pinto, P. Pacheco, J.V. Coelho, E. Lorencon, J.D. Ardisson, J.D. Fabris, P.P. de Souza, K.W.H. Krambrock, L.C.A. Oliveira, M.C. Pereira, Nanostructured δ-FeOOH: an efficient Fenton-like catalyst for the oxidation of organics in water, *Appl. Catal. B-Environ.* 119 (2012) 175–182.
- [26] W. Du, Y. Xu, Y. Wang, Photoinduced degradation of orange II on different iron (Hydr)oxides in aqueous suspension: rate enhancement on addition of hydrogen peroxide, silver nitrate, and sodium fluoride, *Langmuir* 24 (2008) 175–181.
- [27] W.J. Li, D.Z. Li, Y.M. Lin, P.X. Wang, W. Chen, X.Z. Fu, Y. Shao, Evidence for the active species involved in the photodegradation process of methyl orange on TiO₂, *J. Phys. Chem. C* 116 (2012) 3552–3560.
- [28] J. Sheng, X. Li, Y. Xu, Generation of H₂O₂ and OH radicals on Bi₂WO₆ for Phenol degradation under visible light, *ACS Catal.* 4 (2014) 732–737.
- [29] F. Cardon, W.P. Gomes, On the determination of the flat-band potential of a semiconductor in contact with a metal or an electrolyte from the Mott-Schottky plot, *J. Phys. D Appl. Phys.* 11 (1978) L63–L67.