

Goethite ( $\alpha$ -FeOOH) photocatalytic activity at natural concentrations by the addition of  $\text{H}_2\text{O}_2$  at neutral pH and the simultaneous presence of fluoride and bicarbonate

John J. Alvear-Daza<sup>1</sup>, Janeth Sanabria<sup>2</sup>, Victor A. Castaño-Rodríguez<sup>2</sup>, Alejandra Correa-Betancourt<sup>3</sup>, Silvia Binet<sup>4</sup>, Francisco H. Sánchez<sup>5</sup>, Guillermo A. Muñoz-Medina<sup>5,6</sup>, Héctor M. Gutiérrez-Zapata<sup>2</sup>, Luis R. Pizzio<sup>1</sup>, Julián A. Rengifo-Herrera<sup>1\*</sup>

1. Laboratory of Advanced Oxidation Processes and Photocatalysis (LAPh), Centro de Investigación y Desarrollo en Ciencias Aplicadas “Dr. J.J. Ronco” (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT La Plata, CONICET, 47 No. 257, 1900 La Plata, Buenos Aires, Argentina.

2. Environmental Microbiology and Biotechnology Laboratory, Engineering School of Environmental & Natural Resources, Engineering Faculty, Universidad del Valle - Sede Meléndez, A.A. 25360, Santiago de Cali-Colombia

3. Centro de Investigación de la Caña de Azúcar de Colombia (CENICAÑA), Programa de Procesos de Fábrica, Estación Experimental vía Cali-Florida

4. École Polytechnique Fédérale de Lausanne, Institute of Chemical Sciences and Engineering, Lausanne, CH-1015, Switzerland.

5. Instituto de Física La Plata (IFLP-CONICET), Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), 1900 La Plata, Argentina

6. Universidad Argentina de la Empresa (UADE), Facultad de Arquitectura y Diseño, Ciudad Autónoma de Buenos Aires, Argentina, C.P. C1073AAO

Corresponding author:

\* Julián A. Rengifo-Herrera (julianregifo@quimica.unlp.edu.ar)

Tel: +54-221 4211353

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/appl.202300015.

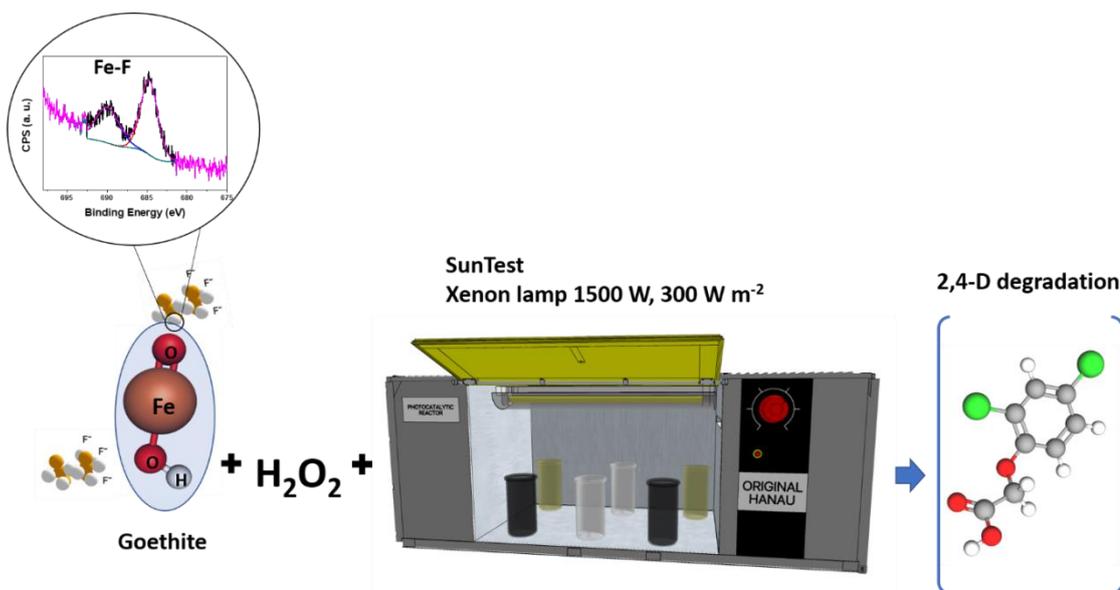
This article is protected by copyright. All rights reserved.

## Abstract

The effect of the simultaneous presence of fluoride (0.15-1.2 mg L<sup>-1</sup>), bicarbonates (83.6-596 mg L<sup>-1</sup>), and synthesized goethite (0.3 mg L<sup>-1</sup>) at typical concentrations often found in groundwater samples was evaluated on the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) at pH 6.9 under simulated sunlight irradiation (300 W m<sup>-2</sup>) and H<sub>2</sub>O<sub>2</sub> concentrations of 10 mg L<sup>-1</sup>. The 2,4-D removal was strongly enhanced by the presence of fluoride. F<sup>-</sup> could modify the surface of iron (hydr)oxide, leading to the formation of surface Fe-F bonds benefiting the formation of free <sup>•</sup>OH, producing upward band bending, reducing the electron-hole recombination, and enhancing the electron transfer to H<sub>2</sub>O<sub>2</sub>. On the other hand, bicarbonate may react with <sup>•</sup>OH generating CO<sub>3</sub><sup>•-</sup> species that could participate in pollutant oxidation, while solar light-induced H<sub>2</sub>O<sub>2</sub> photolysis also played an important role in removing 2,4-D. These findings suggest that tuning of iron (hydr)oxides by fluoride could take place in real groundwater, generating photocatalysts with a high activity that could participate, by adding H<sub>2</sub>O<sub>2</sub>, in the enhancement of sunlight photoinduced natural abiotic processes for pollutant abatement.

### Graphical abstract text

Goethite and fluoride at concentrations typically found in natural waters may produce goethite fluorination leading to an increase of its photocatalytic activity, while the reaction between photoinduced <sup>•</sup>OH and bicarbonate could lead to the formation of carbonate radicals that may exhibit an interesting oxidizing power to degrade 2,4-D as well.



**Keywords:** Goethite, 2,4-dichlorophenoxyacetic acid, pollutant removal, photocatalysis, heterogeneous photo-Fenton reaction

## 1. Introduction

Due to geochemical processes groundwater has interesting physicochemical characteristics such as the presence of bicarbonate, fluorine, and colloidal iron, the latter in the form of (hydr)oxides such as goethite ( $\alpha\text{-FeOOH}$ ) and lepidocrocite ( $\gamma\text{-Fe-OOH}$ ) [1]. Abiotic photoinduced processes involving such species and dissolved organic matter (DOM) could lead to the formation of reactive oxygen species (ROS) such as hydroxyl radicals ( $\cdot\text{OH}$ ) ( $E^\circ = 2.7 \text{ V vs. NHE}$ ) that would be responsible for organic pollutant removal in sunlight irradiated surface and well waters [2–4]. However, the concentration of solar light photoinduced  $\cdot\text{OH}$  radicals in surface waters is low ( $\sim 10^{-17} \text{ mol L}^{-1}$ ) [5], so their effect on the degradation of contaminants would be negligible. For this reason, it is necessary to find strategies to enhance abiotic photoinduced processes in real waters, aiming at the removal of chemical and microbiological pollutants, thus altering the water environment as little as possible. The addition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to groundwater

samples has been explored by our group, exhibiting a promising result to achieve bacteria inactivation and the removal of organic pollutants [6–8].

Goethite is a visible light-absorbing iron (hydr)oxide with apparent promising photocatalytic activity to remove both bacteria and organic pollutants from water [9–16]. However, despite these interesting photocatalytic features, some authors have argued that goethite exhibits high electron-hole recombination since its conduction band potential is too positive (+0.24 V vs. NHE at pH 7.0) compared, for example, with that of molecular oxygen (-0.33 V vs. NHE), preventing an efficient electron transfer and thus increasing charge carrier recombination [17,18].

Interestingly, Du et al. [19] reported for the first time that photocatalytic activities of several iron (hydr)oxides such as goethite and lepidocrocite at concentrations of 0.5 g L<sup>-1</sup> were strongly enhanced by the presence of fluorine amounts ranging between 8.5 and 85 mg L<sup>-1</sup>. The authors claimed that fluorine could alter the surface properties of iron (hydr)oxides. In previous studies of our group, it was found that both 2,4-D (one of the herbicides most widely used around the world and frequently found in drinking water samples [20]) degradation and bacteria inactivation in natural well waters by the addition of H<sub>2</sub>O<sub>2</sub> (10 mg L<sup>-1</sup>) under simulated sunlight irradiation was strongly enhanced by the presence of amounts of fluoride typically found in well waters (0.1-1.2 mg L<sup>-1</sup>) [6,8,21]. Since fluoride and goethite are often found in groundwater samples, their mutual contact in these waters may induce fine-tuning, leading to the generation of fluoridated iron (hydr)oxides with probably enhanced photocatalytic activities. In addition, the presence of other anions in these waters such as bicarbonates may have an important effect since, they can react with <sup>•</sup>OH yielding a less oxidative carbonate radical (CO<sub>3</sub><sup>•-</sup>) (E°= 1.78 V vs. NHE) that would also be able to participate in the

degradation of organic pollutants [22]. These findings demonstrate that the chemical matrix of groundwater could play an important role in the removal of organic pollutants or bacteria from waters photoinduced by a goethite/H<sub>2</sub>O<sub>2</sub> system or pristine goethite.

In this sense, photoinduced removal of 2,4-D by goethite ( $\alpha$ -FeOOH) at concentrations found in well waters (0.3 mg L<sup>-1</sup>) by addition of H<sub>2</sub>O<sub>2</sub> at neutral pH and the simultaneous presence of fluoride and bicarbonate, in amounts typically found in these samples, was evaluated. The results demonstrated that only the addition of hydrogen peroxide to natural groundwater samples is necessary to carry out photo-Fenton-like, H<sub>2</sub>O<sub>2</sub> UVB photolysis and photocatalytic processes able to effectively remove organic contaminants in real waters and how fluoride and bicarbonate ions affect the degradation reaction. This fact may avoid the use of iron salts, photocatalysts or complexing agents in natural groundwater samples, as is commonly reported. The effect of fluoride and bicarbonate concentrations often found in groundwater samples on 2,4-D removal at pH 6.9 under simulated sunlight irradiation and the simultaneous presence of H<sub>2</sub>O<sub>2</sub> and goethite was studied by using a response surface model (RSM) of screening factorial design 2<sup>2</sup> type.

## **2 Experimental Section**

### *2.1 Chemicals*

Chemicals, including ferrous sulfate (FeSO<sub>4</sub>•7H<sub>2</sub>O, Carlo Erba), sodium hydroxide (NaOH, Carlo Erba), acetonitrile (Sigma-Aldrich), 2,4-dichlorophenoxyacetic acid (2,4-D, Sigma-Aldrich), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Carlo Erba), sodium fluoride (NaF, Sigma-Aldrich), sodium bicarbonate (NaHCO<sub>3</sub>, Sigma-Aldrich), and

deionized/demineralized water were used to perform all the experiments. All the reagents were of analytic grade and used without further purification.

## 2.2 Synthesis of goethite

Goethite synthesis followed the procedure reported by Encina et al. [23] with some changes. In short, 5.5 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was dissolved in 100 mL of distilled water. The solution pH was adjusted to 7.0 by the addition of NaOH ( $1.0 \text{ mol L}^{-1}$ ) under continuous stirring. Then, the solution was aerated with a constant flow of oxygen for 60 min until the suspended material became reddish. Finally, the solution was centrifuged for 5 min at 4000 rpm separating the solid, which was then dried at 60 °C for 24 h.

## 2.3 Characterization

Goethite was characterized by Mössbauer spectroscopy at room temperature using a conventional transmission Mössbauer spectrometer in constant acceleration mode, equipped with a 0.3 mCi  $^{57}\text{CoRh}$  source. The spectrometer was calibrated using a 12  $\mu\text{m}$  thick pure Fe foil. X-ray photoelectron spectroscopy (XPS) analyses were carried out with Kratos Axis Ultra XPS analyzer with a monochromatic  $\text{AlK}\alpha$  source and charge neutralizer; diffuse reflectance spectroscopy (DRS) of the samples was recorded using a Perkin-Elmer UV-vis Lambda 35 spectrophotometer equipped with a diffuse reflectance chamber Labsphere RSA-PE-20;  $\text{N}_2$  adsorption-desorption isotherms at -196 °C were used for the textural analysis of the goethite, applying the BET method and using Micromeritics ASAP 2020 equipment, and X-ray diffraction (XRD) patterns were recorded using Philips PW 1732 diffractometer equipped with  $\text{CuK}\alpha$  radiation, nickel filter, 20 mA and 40 kV in the high voltage source.

#### 2.4 Photocatalytic experiments

Experiments were performed using Milli-Q water (in Pyrex glass bottles with a volume of 80 mL) containing 0.3 mg L<sup>-1</sup> (0.2 mg L<sup>-1</sup> of total iron) of goethite and fluoride (0.15-1.20 mg L<sup>-1</sup>), and bicarbonate (83.6-596.0 mg L<sup>-1</sup>) concentrations typically found in well waters at initial pH 6.9; this solution was stirred overnight. Then, 10 mg L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> and 30 mg L<sup>-1</sup> of 2,4-D were spiked under constant magnetic stirring on the sample and irradiated by a Hanau Suntest (AM-1) solar simulator (total intensity: 300 W m<sup>-2</sup>). The lamp has a spectral distribution with about 0.5% of emitted photons at wavelengths shorter than 300 nm (UV-C range) and about 4% between 300 and 400 nm (UVB and UV-A ranges). The distribution of the photons emitted between 400 and 800 nm follows the solar spectrum. The radiant flux was monitored with a Photo-radiometer (HD 2102.2, Delta Ohm). The temperature of the experiments was never higher than 38 °C. Samples were periodically collected to follow the 2,4-D concentration by HPLC (LC20AT, Shimadzu) using, as mobile phase, acetonitrile (55%), an aqueous solution of acetic acid at pH 3.0 (30%), and Milli-Q water (15%) and an HPLC column C-18 Nucleosil 100–5. An isocratic flux of 0.8 mL min<sup>-1</sup> and a UV detector at 280 nm were used. The final pH was monitored in all experiments, reaching a value of 7.5. Experiments were performed in triplicate, and their average was reported. Although the initial 2,4-D concentration is not representative of contaminants of emerging concern (CECs) in water, it was chosen to allow an adequate detection by HPLC equipment available in the laboratory.

To study how different fluoride (F<sup>-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) concentrations typically found in natural groundwater samples could affect the 2,4-D degradation, photoinduced experiments were carried out according to previous work reported by

Gutiérrez-Zapata et al. [21]. A factorial experimental design  $2^2$  was used to study the significant influence of two experimental factors: (A)  $F^-$  and (B)  $HCO_3^-$  concentrations, evaluated in the two levels, low (-) and high (+), which are often found in well waters, on the degradation of 2,4-D pesticide in the presence of natural goethite concentrations ( $0.3 \text{ mg L}^{-1}$ ;  $0.2 \text{ mg L}^{-1}$  of total iron) and  $H_2O_2$  ( $10 \text{ mg L}^{-1}$ ) at pH 6.9. The experimental matrix is presented in Table 1. Additionally, control experiments such as dark reactions (Fenton), 2,4-D photolysis, and sunlight  $H_2O_2$  photolysis were also performed. Results were analyzed using variance analysis (ANOVA) and response surface plots obtained by STATGRAPHICS centurion XVI software.

### *2.5 Determination of total iron by atomic absorption spectroscopy*

Dissolved total iron concentration was measured by flame atomic absorption spectroscopy (AAS) with a Shimadzu AA-7000 equipped with a graphitic oven, at  $\lambda = 248.3 \pm 0.2 \text{ nm}$  (LoQ =  $0.027 \text{ } \mu\text{g L}^{-1}$ ). Aliquots of 25 mL were filtered (membranes of  $0.22 \text{ } \mu\text{m}$ ) and acidified (pH 2.0) for further analysis.

## **3 Results and Discussion**

### *3.1 Goethite physicochemical characterization*

Goethite was synthesized in the laboratory to be used to simulate the iron (hydr)oxide often present in groundwater and was characterized by several techniques to confirm its structure. The XRD pattern of synthesized goethite (Figure 1a) exhibited peaks at  $21.22^\circ$ ,  $33.16^\circ$ ,  $34.71^\circ$ ,  $36.67^\circ$ ,  $41.27^\circ$ ,  $53.29^\circ$ , and  $59.09^\circ$  ascribed to the presence of  $\alpha\text{-FeOOH}$  (JCPDS-29-0713) [24–27].

Figure 1b shows SEM micrographs at 2000x and EDS spectrum of synthesized goethite revealing irregular flake-shape morphology and the presence of surface iron, oxygen, and carbon.

The XPS survey spectrum (Figure 2a) revealed the presence of signals attributed to Fe 2p, C 1s (due to adventitious carbon), O 1s, and S 2p (coming from residual FeSO<sub>4</sub>), while the high-resolution spectrum of Fe 2p (Figure 2b) exhibited two signals at 711.6 and 725.8 eV often assigned to Fe<sup>3+</sup> 2p<sub>3/2</sub> and Fe<sup>3+</sup> 2p<sub>1/2</sub> in goethite [27–29].

Mössbauer measurements (Figure 3a) showed an asymmetric sextet with broadened lines, a hyperfine magnetic field ( $B_{\text{hf}}$ ) around 33 T, and a quadrupole splitting (QS) of 0.45 mm s<sup>-1</sup> matching very well goethite structure [25–27]. Broadened lines and asymmetry could be related to poor crystallinity, as was confirmed by XRD patterns and the presence of Fe(II) [28] respectively, the latter coming from synthesis precursor FeSO<sub>4</sub>. DRS spectrum revealed a broad UV-vis light absorption comprised between 300 and 700 nm, typical of iron (hydr)oxides such as goethite (Figure 3b). The goethite valence band consists of O 2p and occupied Fe 3d orbitals, while its conduction band is composed of unoccupied Fe 3d orbitals. Both bands are separated by a band gap energy of 2.7 eV [31][18].

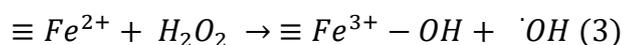
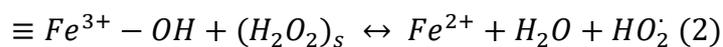
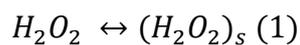
N<sub>2</sub> adsorption-desorption isotherms showed a typical type IV isotherm with hysteresis cycle H-3 corresponding to mesoporous materials according to the IUPAC convention, an average pore width around 16 nm (Figure 4) and BET specific surface area of 98.31 m<sup>2</sup> g<sup>-1</sup>. Similar textural features have also been reported for goethite [29].

### *3.2 Degradation of 2,4-D photoinduced by H<sub>2</sub>O<sub>2</sub>/goethite system in the presence of fluoride and bicarbonates at natural concentrations*

Fenton-like, photo-Fenton-like, and photocatalytic processes were carried out with the concentrations of goethite ( $\alpha$ -FeOOH) often found in well waters ( $0.3 \text{ mg L}^{-1}$ ) in the presence of H<sub>2</sub>O<sub>2</sub> ( $10 \text{ mg L}^{-1}$ ), and the effect of concentrations of fluoride ( $1.2 \text{ mg L}^{-1}$ ) and bicarbonate ( $86 \text{ mg L}^{-1}$ ) was evaluated (Figure 5).

2,4-D at concentrations of  $30 \text{ mg L}^{-1}$  did not undergo degradation in water containing HCO<sub>3</sub><sup>-</sup> ( $86 \text{ mg L}^{-1}$ ) and F<sup>-</sup> ( $1.2 \text{ mg L}^{-1}$ ) by simulated sunlight irradiation (Figure 5: HCO<sub>3</sub><sup>-</sup>/F<sup>-</sup>/SL). As we have already reported [30] under UVB, UVA, and visible light irradiation, 2,4-D concentration was not strongly reduced in milli-Q water, suggesting that photolysis of this molecule did not play an important role.

Although Lin and Gurol [31] claimed that heterogeneous Fenton reactions could take place in goethite/H<sub>2</sub>O<sub>2</sub> systems yielding hydroxyl ( $\cdot\text{OH}$ ) and peroxy ( $\text{HO}_2\cdot$ ) radicals, the former being able to oxidize organic molecules ( $E^\circ = 2.31 \text{ V vs. NHE}$ ) and the latter with a lower oxidizing power [32], our dark experiments showed that in the presence of goethite ( $0.3 \text{ mg L}^{-1}/0.2 \text{ mg L}^{-1}$  of total iron), H<sub>2</sub>O<sub>2</sub> ( $10 \text{ mg L}^{-1}$ ) and anions (F<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>), 2,4-D concentration was not reduced (Figure 5: G/F<sup>-</sup>/HCO<sub>3</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub>/Dark, where G: goethite). In the aforementioned report, the authors suggested that, in dark conditions, H<sub>2</sub>O<sub>2</sub> could be adsorbed onto goethite surfaces and undergo further decomposition yielding  $\cdot\text{OH}$  and  $\text{HO}_2\cdot$  (Eq. 1-3) (heterogeneous Fenton reaction). The low concentrations of goethite used herein would be responsible for the minor role played by heterogeneous Fenton reaction. Moreover, the dark adsorption of 2,4-D on goethite (G/Dark) was found to be negligible.

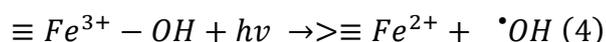


Photocatalytic reactions under sunlight irradiation of goethite (in the absence of  $H_2O_2$ ) in the presence or absence of anions led to a 2,4-D degradation of 10% after 240 min (Figure 5: G/SL; G/F/ $HCO_3^-$ /SL). As was described above,  $\alpha$ -FeOOH does not show an important photocatalytic behavior since its conduction band potential is very positive and unable to reduce molecular oxygen, leading to the high  $e^-/h^+$  pair recombination [17,18], despite some authors have argued that goethite seems to be a promising photocatalyst to remove several organic pollutants such as dyes, chlorophenols, and polycyclic aromatic hydrocarbons [11,33–35]. However, in these aforementioned studies, goethite concentrations ranged from 1 to 500 g L<sup>-1</sup> (herein a concentration of 0.0003 g L<sup>-1</sup> was used) and the high pollutant removal rates observed may probably be directly related to high photocatalyst concentrations. In addition, the photocatalytic reaction did not change in the presence of bicarbonate and fluoride.

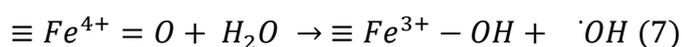
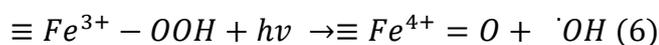
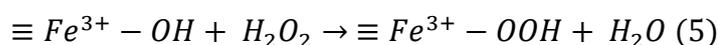
Otherwise, when 10 mg L<sup>-1</sup> of  $H_2O_2$  was added to water containing goethite (photo-Fenton-like/photocatalytic reactions) and bicarbonate at initial pH 6.9 under simulated sunlight irradiation, 2,4-D concentration was strongly reduced (75%) after 240 min of simulated sunlight irradiation (Figure 5: G/ $HCO_3^-$ / $H_2O_2$ /SL). Several authors have reported the positive effect of  $H_2O_2$  addition to  $\alpha$ -FeOOH photocatalytic systems to degrade several pollutants [36,37]. Nevertheless, these studies were performed using  $\alpha$ -FeOOH and  $H_2O_2$  concentrations of 1 g L<sup>-1</sup> and 50-

170 mg L<sup>-1</sup> respectively, which are much higher than the natural amounts of goethite (0.0003 g L<sup>-1</sup>) and H<sub>2</sub>O<sub>2</sub> (10 mg L<sup>-1</sup>) used herein.

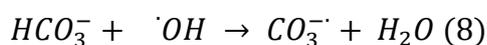
On the other hand, under sunlight irradiation, surface ≡ Fe<sup>2+</sup> species could be photoinduced (Eq. 4) [36]. These species could react with H<sub>2</sub>O<sub>2</sub>, leading to the generation of surficial/surface ≡ Fe<sup>3+</sup> and extra ·OH radicals (heterogeneous photo-Fenton reaction) (Eq. 4).



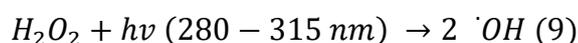
Furthermore, by UV-vis light irradiation surface ≡ Fe<sup>3+</sup> - OOH species generated by H<sub>2</sub>O<sub>2</sub> adsorption on goethite surface (Eq. 5) could, form photoinduced ferryl species (≡ Fe<sup>4+</sup> = O) (Eq. 6), the latter being very unstable in aqueous solutions, also leading to the formation of ·OH (Eq. 7) [38].



Bicarbonates (83.6 mg L<sup>-1</sup>), which were also present at typical concentrations often found in natural waters by regulating the pH at 6.9, could react with ·OH generating carbonate radicals (CO<sub>3</sub><sup>·-</sup>) (Eq. 8) that are able to remove 2,4-D as well [39,40]. CO<sub>3</sub><sup>·-</sup> could participate in electron transfer and H-abstraction reactions, leading to the oxidation of organic molecules [22]. All these routes mentioned above could be responsible for the significant removal of 2,4-D in the presence of bicarbonate.

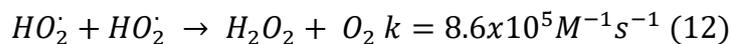
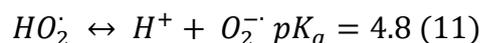
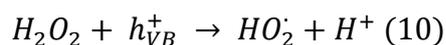


Surprisingly, experiments where only hydrogen peroxide, fluoride, and bicarbonate were present (in the absence of goethite) at concentrations of 10, 83.6, and 1.2 mg L<sup>-1</sup>, respectively, under simulated sunlight irradiation at initial pH 6.9, exhibited a strong 2,4-D removal of around 85% after 240 min (Figure 5: H<sub>2</sub>O<sub>2</sub>/F<sup>-</sup>/HCO<sub>3</sub><sup>-</sup>/SL). As has been suggested, sunlight or UVB light irradiation can photoinduce H<sub>2</sub>O<sub>2</sub> photolysis (Eq. 9) [7,30]. Pyrex-glass reactors used can allow the transmission of UVB light coming from the solar simulator to a lesser extent, leading to H<sub>2</sub>O<sub>2</sub> photolysis.



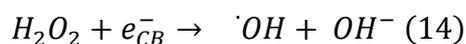
The experiments of H<sub>2</sub>O<sub>2</sub> photolysis without anions (H<sub>2</sub>O<sub>2</sub>/SL) revealed that 2,4-D degradation underwent a slight reduction. Perhaps, bicarbonate reaction with  $\cdot OH$  leading to the generation of CO<sub>3</sub><sup>-</sup> could be the reason for the observed enhancement (Eq. 8).

The photocatalytic experiment in the absence of fluoride (G/HCO<sub>3</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub>/SL) showed evidence that goethite could affect the  $\cdot OH$  production by H<sub>2</sub>O<sub>2</sub> photolysis. Two phenomena could be responsible for this detrimental effect: First, H<sub>2</sub>O<sub>2</sub> oxidation (+1.06 V vs. NHE) [41] by photoinduced goethite valence band holes (VB oxidation potential: +2.3 V vs. NHE [18]) could also take place, producing peroxy radical (HO<sub>2</sub> $\cdot$ ) (Eq. 10; Figure 7) unable to oxidize 2,4-D. The peroxy radical is in equilibrium with anion superoxide radical (O<sub>2</sub><sup>-</sup>) (Eq. 11) and its pK<sub>a</sub> is around 4.8, so at pH higher than pK<sub>a</sub> (pH during the experiments increased from 6.9 to 7.5) the anion superoxide radical will be the main species in solution that undergoes a fast disproportionation, leading to the generation of H<sub>2</sub>O<sub>2</sub> (Eqs. 12-13) [42][43].



Second, goethite exhibits an important UV light absorption (Figure 3b), possibly causing a screen effect and competing with H<sub>2</sub>O<sub>2</sub> molecules for UVB photons.

Another pathway for ROS generation could be H<sub>2</sub>O<sub>2</sub> direct reduction by goethite CB photoinduced electrons. Since the hydrogen peroxide reduction potential is +0.32 V (vs. NHE) and photoinduced conduction band electrons in goethite may have a redox potential of +0.24 V (vs. NHE) [44], it is expected that H<sub>2</sub>O<sub>2</sub> reduction by goethite CB photoinduced electrons will take place leading to the generation of hydroxyl radicals (Eq. 14).



As was expected, when the amounts of fluoride typically found in well waters (1.2 mg L<sup>-1</sup>) were added to water already containing bicarbonates (83.6 mg L<sup>-1</sup>) in the presence of goethite and H<sub>2</sub>O<sub>2</sub> (10 mg L<sup>-1</sup>), the 2,4-D degradation increased markedly, reaching 95% in 240 min of simulated sunlight irradiation (Figure 5: G/F/HCO<sub>3</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub>/SL). XPS measurements of goethite separated from the aqueous solution after the reaction confirmed the presence of fluoride in goethite (1.2 at%) (Figure 6a), and a high-resolution F 1s spectrum (Figure 6b) revealed the presence of two signals at 684.7 eV and 689.5 eV often linked to the presence of adsorbed fluoride in iron (hydr)oxides and Fe-F bonds respectively [43].

Hiemstra and Van Riemsdijk [43] concluded that fluoride adsorption onto goethite is achieved on several surface sites and is favored at acidic pH values (goethite isoelectric point: 7.9). Moreover, by theoretical calculations the authors suggested that the formation of surface Fe-F bonds would be feasible. On the other hand, Ding et al. [44] corroborated that the highest fluoride adsorption was obtained at acid pH values and proposed that fluoride adsorption may be achieved by exchange with surface -OH groups.

As was mentioned above, the beneficial effect of fluoride presence on photocatalytic degradation using goethite and lepidocrocite was first claimed by Du et al. [19]. The use of 8.5-85 mg L<sup>-1</sup> fluoride increased the photocatalytic degradation of orange II dye at pH 6.5 by irradiation of these iron (hydr)oxides (0.5 g L<sup>-1</sup>). The authors suggested that fluoride could modify the surface of iron (hydr)oxides increasing the production of  $\cdot\text{OH}$ ; however, the mechanism was not proposed. Meanwhile, on TiO<sub>2</sub> a mechanism was suggested. In the literature there are several studies suggesting different mechanisms to find out how fluoride anions could enhance the photocatalytic activity of metal oxide semiconductors such as TiO<sub>2</sub>. For instance, Minella et al. [45] and Deskins and coworkers [46] suggested that the flat band potential of semiconductors may be fine-tuned by surface anion adsorption. This flat band modification will depend on the nature and density of ions, while Montoya and Salvador found that TiO<sub>2</sub> fluorination produced a negative flat-band shift of around 80 mV [47] compatible with upward band bending in semiconductors by an excess of negative charge surface. Other authors have also described this behavior in fluoridated TiO<sub>2</sub> nanoparticles, suggesting that the exchange of surface -OH groups by F atoms on TiO<sub>2</sub> (formation of surface Ti-F bonds) may decrease the formation of deeply trapped holes, favoring less deep

surface trapping sites and making faster the electron transfer of photoinduced holes to phenol molecules [48]. However, Xu et al. proposed a new theory suggesting that fluoride ions present in the Helmholtz layer can induce the desorption of photoinduced surface-bound  $\cdot\text{OH}$  in  $\text{TiO}_2$  surfaces through a fluorine hydrogen bond.

Thus, it is possible to suggest that in the presence of fluoride (at concentrations typically found in groundwater)  $\alpha\text{-FeOOH}$  surfaces can be superficially modified leading to either/both upward band bending (Figure 7a) or/and enhanced generation of free hydroxyl radicals upon sunlight irradiation (Figure 7b). Upward band bending could enhance  $\text{H}_2\text{O}_2$  reduction by photoinduced conduction band electrons in goethite (Eq. 14), yielding  $\cdot\text{OH}$  more efficiently, and thus enhancing the photocatalytic degradation of 2,4-D, as was observed.

The effect of homogeneous photo-Fenton reactions was also assessed since iron (hydr)oxides can often undergo photoinduced iron dissolution in water [49,50]. Factors such as acidic pH and the presence of aliphatic acids such as oxalate can also enhance iron dissolution by forming soluble ferric-oxalate complexes at circumneutral pH. For this reason, herein photocatalytic experiments were not carried out in the absence of bicarbonates, since under these conditions, the pH of the solution dropped to about 4.0, promoting goethite dissolution. The presence of dissolved iron either complexed or not can induce homogeneous photo-Fenton reactions in the presence of hydrogen peroxide [51]. In our experimental conditions, the final pH of the reaction was always around 7.5, confirming that 2,4-D removal was achieved at neutral/basic pH. The presence of dissolved iron was evaluated by atomic absorption spectroscopy measurements of the supernatant obtained by further 0.22  $\mu\text{m}$  filtration after the photochemical and Fenton-like

reactions. In dark experiments, the total iron concentration was  $2.81 \mu\text{g L}^{-1}$ , while the simulated sunlight-irradiated experiment in the absence of hydrogen peroxide showed an iron concentration of  $2.9 \mu\text{g L}^{-1}$ . The simultaneous presence of goethite, anions ( $\text{F}^-$  and  $\text{HCO}_3^-$ ),  $\text{H}_2\text{O}_2$ , and simulated sunlight exhibited an iron concentration of  $11 \mu\text{g L}^{-1}$ . These iron amounts are too low to induce Fenton or photo-Fenton reactions at neutral pH to generate appreciable concentrations of  $\cdot\text{OH}$  responsible for herbicide removal, pointing out that the degradation was mainly due to heterogeneous photo-Fenton processes/sunlight  $\text{H}_2\text{O}_2$  photolysis.

### *3.3 Evaluation of the effect of fluoride and bicarbonate concentration on 2,4-D photoinduced degradation under simulated sunlight irradiation by a factorial experimental design*

A factorial design  $2^2$  was used to study the effect of natural concentrations of fluoride ( $0.15\text{-}1.2 \text{ mg L}^{-1}$ ) and bicarbonates ( $83.6\text{-}596.0 \text{ mg L}^{-1}$ ) typically found in groundwater samples on simulated sunlight-irradiated goethite ( $0.3 \text{ mg L}^{-1}$ ;  $0.2 \text{ mg L}^{-1}$  of total iron) degradation of 2,4-D ( $30 \text{ mg L}^{-1}$ ) in the presence of  $10 \text{ mg L}^{-1}$  of  $\text{H}_2\text{O}_2$  at pH 6.9 after 90 min of sunlight irradiation. ANOVA results confirmed a polynomial equation of second order with  $R^2=99.87$  and  $P\text{-value}<0.05$ .

Surface response (Figure 8a) shows that with increasing fluoride and bicarbonate concentrations, the 2,4-D removal rises as well. The Pareto chart (Figure 8b) revealed that the presence of fluoride at its maximum level ( $1.2 \text{ mg L}^{-1}$ ) plays a significant role. Moreover, the combined interaction of bicarbonates and fluoride at their maximum levels ( $596.0 \text{ mg L}^{-1}$  and  $1.2 \text{ mg L}^{-1}$  respectively) also had an important role in herbicide degradation. This was corroborated in Figure 8c where the factor interaction chart is shown, and it was observed that high bicarbonate and fluoride concentrations exhibited a high 2,4-D degradation.

Results suggest that fluoride and bicarbonate at concentrations typically found in groundwater samples could have a positive effect on the 2,4-D removal using goethite at low concentrations by adding  $\text{H}_2\text{O}_2$  doses of  $10 \text{ mg L}^{-1}$  under simulated sunlight irradiation. This finding has important environmental implications since the simple addition of hydrogen peroxide to groundwater samples upon natural sunlight irradiation may enhance several photoinduced phenomena involving fluorinated and colloidal iron for the removal of organic pollutants or bacteria inactivation.

### **Conclusions**

Fluoride, iron (hydr)oxide such as goethite, and bicarbonate at concentrations typically found in groundwater samples could play an important role in sunlight photoinduced reactions in the presence of  $\text{H}_2\text{O}_2$  ( $10 \text{ mg L}^{-1}$ ) for the abatement of organic pollutants. We suggest that goethite fluorination may take place leading to an increase of iron (hydr)oxide photocatalytic activity, while the reaction between photoinduced  $\cdot\text{OH}$  and bicarbonate ( $\text{HCO}_3^-$ ) could lead to the formation of carbonate radicals ( $\text{CO}_3^{\cdot-}$ ) that may exhibit an interesting oxidizing power to degrade 2,4-D molecules as well.

The implications of these findings are very important since abiotic sunlight photoinduced processes could be enhanced by the simple addition of hydrogen peroxide to remove both organic pollutants and bacteria from groundwater samples without the further addition of iron salts, photocatalysts, and complexing agents. Moreover, results also suggest that goethite fluorination in real groundwater could lead to the formation of iron (hydr)oxides with enhanced photocatalytic activities.

### **Acknowledgments**

The authors thank “Fondo de Ciencia, Tecnología e Innovación del Sistema General de Regalías de Colombia” for the economic support (grant BPIN2014000100031). J.A. Rengifo-Herrera and L.R. Pizzio are grateful to “Consejo Nacional de Investigaciones Científicas y Técnicas”-CONICET and National University of La Plata, UNLP, Argentina, for the economic support (grants PIP 1492 and PIO 024).

### **Conflict of Interest Statement**

The authors declare no conflict of interest.

### **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

### **References**

- [1] C. Appelo, D. Postma, *Geochemistry, Groundwater and Pollution*, Second, Taylor & Francis, Amsterdam, 2005.
- [2] S. Gligorovski, R. Strekowski, S. Barbati, D. Vione, Environmental Implications of Hydroxyl Radicals ( $\cdot\text{OH}$ ), *Chem Rev.* 115 (2015) 13051–13092.  
<https://doi.org/10.1021/cr500310b>.
- [3] F.J. Millero, S. Sotolongo, The oxidation of Fe(II) with  $\text{H}_2\text{O}_2$  in seawater, *Geochim Cosmochim Acta.* 53 (1989) 1867–1873.  
[https://doi.org/10.1016/0016-7037\(89\)90307-4](https://doi.org/10.1016/0016-7037(89)90307-4).
- [4] S. Rahim Pouran, A.A. Abdul Raman, W.M.A. Wan Daud, Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions, *J Clean Prod.* 64 (2014) 24–35.  
<https://doi.org/10.1016/j.jclepro.2013.09.013>.
- [5] T. Mill, D. Hendry, H. Richardson, Free-radical oxidants in natural waters, *Science* (1979). 207 (1980) 886–887.

- [6] H.M. Gutiérrez-Zapata, J.J. Alvear-Daza, J.A. Rengifo-Herrera, J. Sanabria, Addition of Hydrogen Peroxide to Groundwater with Natural Iron Induces Water Disinfection by Photo-Fenton at Circumneutral pH and other Photochemical Events, *Photochem Photobiol.* 93 (2017) 1224–1231. <https://doi.org/10.1111/php.12779>.
- [7] J.L. Buitrago, J. Sanabria, H.M. Gutiérrez-Zapata, F.J. Urbano-Ceron, A. García-Barco, P. Osorio-Vargas, J.A. Rengifo-Herrera, Photo-Fenton process at natural conditions of pH, iron, ions, and humic acids for degradation of diuron and amoxicillin, *Environmental Science and Pollution Research.* 27 (2020) 1608–1624. <https://doi.org/10.1007/s11356-019-06700-y>.
- [8] J.J. Alvear-Daza, A. García-Barco, P. Osorio-Vargas, H.M. Gutiérrez-Zapata, J. Sanabria, J.A. Rengifo-Herrera, Resistance and induction of viable but non culturable states (VBNC) during inactivation of *E. coli* and *Klebsiella pneumoniae* by addition of H<sub>2</sub>O<sub>2</sub> to natural well water under simulated solar irradiation, *Water Res.* 188 (2021) 116449. <https://doi.org/10.1016/j.watres.2020.116499>.
- [9] L. Mammeri, T. Sehili, S. Belaidi, K. Djebbar, Heterogeneous photodegradation of 1-naphthol with natural iron oxide in water: influence of oxalic acid, *Desalination Water Treat.* 54 (2015) 2324–2333. <https://doi.org/10.1080/19443994.2014.899928>.
- [10] S. Belaidi, T. Sehili, L. Mammeri, K. Djebbar, Photodegradation kinetics of 2,6-dimethylphenol by natural iron oxide and oxalate in aqueous solution, *J Photochem Photobiol A Chem.* 237 (2012) 31–37. <https://doi.org/10.1016/j.jphotochem.2012.03.023>.
- [11] G.B. Ortiz De La Plata, O.M. Alfano, A.E. Cassano, The heterogeneous photo-Fenton reaction using goethite as catalyst, *Water Science and Technology.* 61 (2010) 3109–3116. <https://doi.org/10.2166/wst.2010.258>.
- [12] F.B. Li, X.Z. Li, X.M. Li, T.X. Liu, J. Dong, Heterogeneous photodegradation of bisphenol A with iron oxides and oxalate in aqueous

- solution, *J Colloid Interface Sci.* 311 (2007) 481–490.  
<https://doi.org/10.1016/j.jcis.2007.03.067>.
- [13] E.M. Rodríguez, G. Fernández, P.M. Álvarez, R. Hernández, F.J. Beltrán, Photocatalytic degradation of organics in water in the presence of iron oxides: Effects of pH and light source, *Appl Catal B.* 102 (2011) 572–583.  
<https://doi.org/10.1016/j.apcatb.2010.12.041>.
- [14] N. Murakami, T. Matsuo, T. Tsubota, T. Ohno, Photocatalytic reaction over iron hydroxides: A novel visible-light- responsive photocatalyst, *Catal Commun.* 12 (2011) 341–344.  
<https://doi.org/10.1016/j.catcom.2010.10.012>.
- [15] J. He, W. Ma, W. Song, J. Zhao, X. Qian, S. Zhang, J.C. Yu, Photoreaction of aromatic compounds at  $\alpha$ -FeOOH/H<sub>2</sub>O interface in the presence of H<sub>2</sub>O<sub>2</sub>: Evidence for organic-goethite surface complex formation, *Water Res.* 39 (2005) 119–128.  
<https://doi.org/10.1016/j.watres.2004.09.006>.
- [16] M. Menager, M. Sarakha, Simulated solar light phototransformation of organophosphorus azinphos methyl at the surface of clays and goethite, *Environ Sci Technol.* 47 (2013) 765–772. <https://doi.org/10.1021/es301866f>.
- [17] J.K. Leland, A.J. Bard, Photochemistry of colloidal semiconducting iron oxide polymorphs, *J. Phys. Chem.* 91 (1987) 5076–5083. <https://doi.org/10.1021/j100303a039>.
- [18] D.M. Sherman, Electronic structures of iron(III) and manganese(IV) (hydr)oxide minerals: Thermodynamics of photochemical reductive dissolution in aquatic environments, *Geochim Cosmochim Acta.* 69 (2005) 3249–3255.  
<https://doi.org/10.1016/j.gca.2005.01.023>.
- [19] 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, fluoride. *Langmuir.* (2008) 175–181.  
<http://pubs.acs.org/doi/abs/10.1021/la7021165>.
- [20] World Health Organization, 2,4-D in Drinking-water Background document for development

- of WHO Guidelines for Drinking-water Quality, (2003) 1–17.
- [21] H.M. Gutiérrez-Zapata, K.L. Rojas, J. Sanabria, J.A. Rengifo-Herrera, 2,4-D abatement from groundwater samples by photo-Fenton processes at circumneutral pH using naturally iron present. Effect of inorganic ions, *Environmental Science and Pollution Research*. 24 (2017) 6213–6221. <https://doi.org/10.1007/s11356-016-7067-5>.
- [22] M.L. Dell’Arciprete, J.M. Soler, L. Santos-Juanes, A. Arques, D.O. Mártire, J.P. Furlong, M.C. Gonzalez, Reactivity of neonicotinoid insecticides with carbonate radicals, *Water Res.* 46 (2012) 3479–3489. <https://doi.org/10.1016/j.watres.2012.03.051>.
- [23] E.R. Encina, M. Distaso, R.N. Klupp Taylor, W. Peukert, Synthesis of goethite  $\alpha$ -FeOOH particles by air oxidation of ferrous hydroxide  $\text{Fe}(\text{OH})_2$  suspensions: Insight on the formation mechanism, *Cryst Growth Des.* 15 (2015) 194–203. <https://doi.org/10.1021/cg501191h>.
- [24] S.M. Amininasab, P. Holakoei, Z. Shami, M. Hassanzadeh, Preparation and evaluation of functionalized goethite nanorods coated by molecularly imprinted polymer for selective extraction of bisphenol A in aqueous medium, *Journal of Polymer Research*. 25 (2018). <https://doi.org/10.1007/s10965-018-1481-y>.
- [25] M. Ristić, S. Krehula, M. Reissner, S. Musić,  $^{57}\text{Fe}$  Mössbauer, XRD, FT-IR, FE SEM Analyses of Natural Goethite, Hematite and Siderite, *Croatica Chemica Acta*. 90 (2017) 499–507. <https://doi.org/10.5562/cca3233>.
- [26] W. Salama, M. El Aref, R. Gaupp, Spectroscopic characterization of iron ores formed in different geological environments using FTIR, XPS, Mössbauer spectroscopy and thermoanalyses, *Spectrochim Acta A Mol Biomol Spectrosc.* 136 (2015) 1816–1826. <https://doi.org/10.1016/j.saa.2014.10.090>.
- [27] A. Bustamante, D. Lovera, R. Quille, A. V. Arias, J. Quiñones, Mössbauer spectroscopy study of a mineral sample from Oshno hill, District of Chavín de Parí, Huanuco Region, Peru, *Hyperfine Interact.* 195 (2009)

- 63–68. <https://doi.org/10.1007/s10751-009-0102-x>.
- [28] L. Notini, D.E. Latta, A. Neumann, C.I. Pearce, M. Sassi, A.T. N'diaye, K.M. Rosso, M.M. Scherer, A Closer Look at Fe(II) Passivation of Goethite, *ACS Earth Space Chem.* 3 (2019) 2717–2725. <https://doi.org/10.1021/acsearthspacechem.9b00224>.
- [29] A. Jelle, M. Hmadeh, P. O'Brien, P. D.D, G.A. Ozin, Photocatalytic properties of all four polymorphs of nanostructured iron oxyhydroxides, *ChemNanomat.* 2 (2016) 1047–1054. <https://doi.org/10.1002/cnma.201600251>.
- [30] A. Serra-Clusellas, L. De Angelis, C.H. Lin, P. Vo, M. Bayati, L. Sumner, Z. Lei, N.B. Amaral, L.M. Bertini, J. Mazza, L.R. Pizzio, J.D. Stripeikis, J.A. Rengifo-Herrera, M.M. Fidalgo de Cortalezzi, Abatement of 2,4-D by H<sub>2</sub>O<sub>2</sub> solar photolysis and solar photo-Fenton-like process with minute Fe(III) concentrations, *Water Res.* 144 (2018) 572–580. <https://doi.org/10.1016/j.watres.2018.07.072>.
- [31] S.S. Lin, M.D. Gurol, Catalytic decomposition of hydrogen peroxide on iron oxide: Kinetics, mechanism, and implications, *Environ Sci Technol.* 32 (1998) 1417–1423. <https://doi.org/10.1021/es970648k>.
- [32] Y. Nosaka, A.Y. Nosaka, Generation and Detection of Reactive Oxygen Species in Photocatalysis, *Chem Rev.* 117 (2017) 11302–11336. <https://doi.org/10.1021/acs.chemrev.7b00161>.
- [33] H. Gupta, B. Gupta, Photocatalytic degradation of polycyclic aromatic hydrocarbon benzo[a]pyrene by iron oxides and identification of degradation products, *Chemosphere.* 138 (2015) 924–931. <https://doi.org/10.1016/j.chemosphere.2014.12.028>.
- [34] S. Belattar, N. Debbache, I. Ghoul, T. Sehili, A. Abdessemed, Photodegradation of phenol red in the presence of oxyhydroxide of Fe(III) (Goethite) under artificial and a natural light, *Water and Environment Journal.* 32 (2018) 358–365. <https://doi.org/10.1111/wej.12333>.

- [35] G. Zhang, Q. Wang, W. Zhang, T. Li, Y. Yuan, P. Wang, Effects of organic acids and initial solution pH on photocatalytic degradation of bisphenol A (BPA) in a photo-Fenton-like process using goethite ( $\alpha$ -FeOOH), *Photochem. Photobiol. Sci.* 15 (2016) 1046–1053. <https://doi.org/10.1039/C6PP00051G>.
- [36] Y. Mameri, N. Debbache, N. Seraghni, Heterogeneous photodegradation of paracetamol using Goethite/H<sub>2</sub>O<sub>2</sub> and Goethite/oxalic acid systems under artificial and natural light, *J Photochem Photobiol A Chem.* 315 (2016) 129–137. <https://doi.org/10.1016/j.jphotochem.2015.09.019>.
- [37] C. Ruales-Lonfat, J.F. Barona, A. Sienkiewicz, M. Bensimon, J. Vélez-Colmenares, N. Benítez, C. Pulgarín, Iron oxides semiconductors are efficient for solar water disinfection: A comparison with photo-Fenton processes at neutral pH, *Appl Catal B.* 166–167 (2015) 497–508. <https://doi.org/10.1016/j.apcatb.2014.12.007>.
- [38] J. He, X. Tao, W. Ma, J. Zhao, Heterogeneous Photo-Fenton Degradation of an Azo Dye in Aqueous H<sub>2</sub>O<sub>2</sub>/Iron Oxide Dispersions at Neutral pHs, *Chem Lett.* (2002) 86–86. <https://doi.org/10.1246/cl.2002.86>.
- [39] W. Huang, A. Bianco, M. Brigante, G. Mailhot, UVA-UVB activation of hydrogen peroxide and persulfate for advanced oxidation processes: Efficiency, mechanism and effect of various water constituents, *J Hazard Mater.* 347 (2018) 279–287. <https://doi.org/10.1016/j.jhazmat.2018.01.006>.
- [40] C. Pétrier, R. Torres-Palma, E. Combet, G. Sarantakos, S. Baup, C. Pulgarin, Enhanced sonochemical degradation of bisphenol-A by bicarbonate ions, *Ultrason Sonochem.* 17 (2010) 111–115. <https://doi.org/10.1016/j.ultsonch.2009.05.010>.
- [41] K. Sahel, L. Elsellami, I. Mirali, F. Dappozze, M. Bouhent, C. Guillard, Hydrogen peroxide and photocatalysis, *Appl Catal B.* 188 (2016) 106–112. <https://doi.org/10.1016/j.apcatb.2015.12.044>.

- [42] O.J.M. Bockris, M. Oldfield, The oxidation-reduction reactions of hydrogen peroxide at inert metal electrodes and mercury cathodes, *Transactions of the Faraday Society*. (1955) 249–259.  
<https://doi.org/10.1017/CBO9781107415324.004>.
- [43] T. Hiemstra, W.H. Van Riemsdijk, Fluoride adsorption on goethite in relation to different types of surface sites, *J Colloid Interface Sci*. 225 (2000) 94–104.  
<https://doi.org/10.1006/jcis.1999.6697>.
- [44] X. Ding, X. Song, Identification of Fluoride and Phosphate Binding Sites at FeOOH Surfaces, *The Journal of Physical Chemistry C*. 116 (2012) 21939–21947.  
<https://doi.org/10.1021/jp3083776>.
- [45] M. Minella, V. Maurino, C. Minero, E. Pelizzetti, Thin film nanocrystalline TiO<sub>2</sub> electrodes: Dependence of flat band potential on pH and anion adsorption, *J Nanosci Nanotechnol*. 15 (2015) 3348–3358.  
<https://doi.org/10.1166/jnn.2015.10206>.
- [46] N.A. Deskins, R. Rousseau, M. Dupuis, Defining the role of excess electrons in the surface chemistry of TiO<sub>2</sub>, *Journal of Physical Chemistry C*. 114 (2010) 5891–5897.  
<https://doi.org/10.1021/jp101155t>.
- [47] J.F. Montoya, P. Salvador, The influence of surface fluorination in the photocatalytic behaviour of TiO<sub>2</sub> aqueous dispersions: An analysis in the light of the direct-indirect kinetic model, *Appl Catal B*. 94 (2010) 97–107.  
<https://doi.org/10.1016/j.apcatb.2009.10.025>.
- [48] C. Minero, G. Mariella, V. Maurino, D. Vione, E. Pelizzetti, Photocatalytic Transformation of Organic Compounds in the Presence of Inorganic Ions. 2. Competitive Reactions of Phenol and Alcohols on a Titanium Dioxide-Fluoride, *Langmuir*. 16 (2000) 8964–8972.
- [49] Y. Chen, C.J. Miller, T.D. Waite, Heterogeneous Fenton chemistry revisited: Mechanistic insights from ferrihydrite-mediated oxidation of formate and oxalate, *Environ Sci Technol*. 55 (2021) 14414–14425.  
<https://doi.org/10.1021/acs.est.1c00284>.

- [50] T. Xu, Y. Fang, T. Tong, Y. Xia, X. Liu, L. Zhang, Environmental photochemistry in hematite-oxalate system: Fe(III)-Oxalate complex photolysis and ROS generation, *Appl Catal B.* 283 (2021) 119645. <https://doi.org/10.1016/j.apcatb.2020.119645>.
- [51] L. Clarizia, D. Russo, I. Di Somma, R. Marotta, R. Andreozzi, Homogeneous photo-Fenton processes at near neutral pH: A review, *Appl Catal B.* 209 (2017) 358–371. <https://doi.org/10.1016/j.apcatb.2017.03.011>.

Figure captions

**Figure 1.** (a) XRD pattern of synthesized goethite. (b) SEM micrograph and EDS spectrum of synthesized goethite.

**Figure 2.** Goethite XPS characterization. (a) XPS survey spectrum, (b) Fe 2p<sub>3/2</sub> high-resolution spectrum.

**Figure 3.** a) Goethite Mossbauer spectrum. b) Diffuse reflectance spectrum of synthesized goethite.

**Figure 4.** N<sub>2</sub> adsorption-desorption profile of goethite. The insert indicates the pore volume and diameter distribution.

**Figure 5.** Photocatalytic degradation of 2,4-D (30 mg L<sup>-1</sup>) under simulated sunlight irradiation (300 W m<sup>-2</sup>) and dark conditions in Milli-Q water containing goethite (G) (0.3 mg L<sup>-1</sup>(0.2 mg L<sup>-1</sup> of total iron)), fluoride (1.2 mg L<sup>-1</sup>), bicarbonate (86.3 mg L<sup>-1</sup>), and H<sub>2</sub>O<sub>2</sub> (10 mg L<sup>-1</sup>) at initial pH 6.9. The final pH in all experiments was 7.5. The temperature was not higher than 38 °C. SL: Solar light.

**Figure 6.** Fe 2p<sub>3/2</sub> high-resolution XPS spectrum of goethite in contact with fluoride (1.2 mg L<sup>-1</sup>) after the photocatalytic experiment.

**Figure 7.** Mechanisms of goethite fluorination. (a) Formation of free hydroxyl radicals and presence of two kinds of fluoride species adsorbed on the surface. (b) Upward band bending caused by the adsorption of fluorine anions on goethite surfaces.

**Figure 8.** Factorial experimental design of 2,4-D degradation by goethite ( $0.3 \text{ mg L}^{-1}$  ( $0.2 \text{ mg L}^{-1}$  of total iron)) and  $\text{H}_2\text{O}_2$  ( $10 \text{ mg L}^{-1}$ ) at initial pH 6.9 after 90 min of simulated sunlight irradiation ( $300 \text{ W m}^{-2}$ ) in the presence of low and high amounts of fluoride and bicarbonate often found in natural well waters. (a) Response surface, (b) Pareto chart, and (c) factor interaction chart. The final pH in all experiments was 7.5. The temperature was not higher than  $38 \text{ }^\circ\text{C}$ .

Table captions

**Table 1.** Matrix of factorial experimental design.

Tables

Table 1: Factor	Levels	
	Low (-)	High (+)
A: $\text{F}^-$ ( $\text{mg L}^{-1}$ )	0.15	1.20
B: $\text{HCO}_3^-$ ( $\text{mg L}^{-1}$ )	83.6	596.0
Run	Factor design	
	A	B
1	-	-
2	+	-
3	-	+
4	+	+

Figures

Figure 1

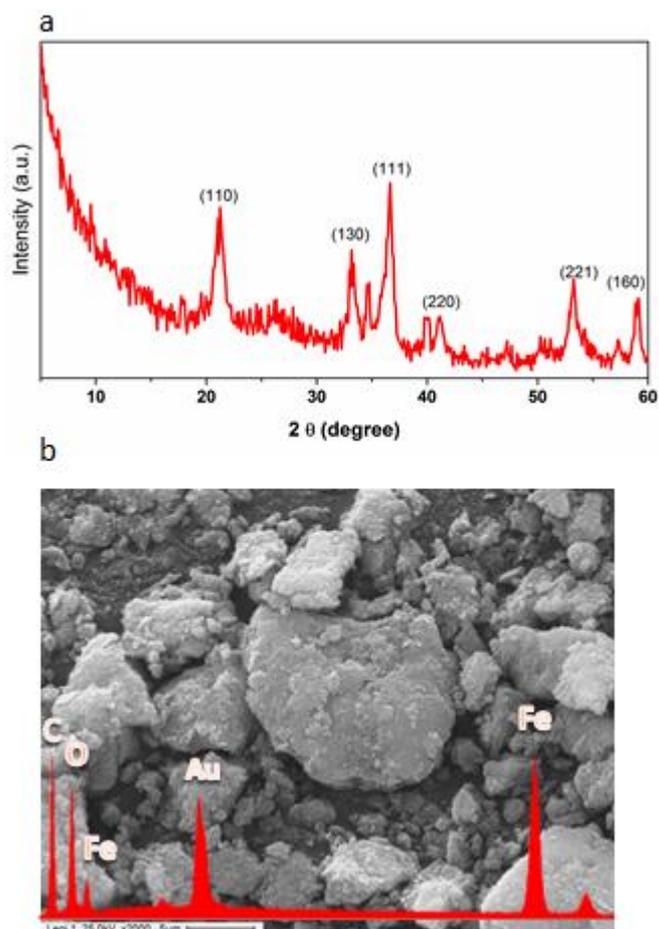


Figure 2

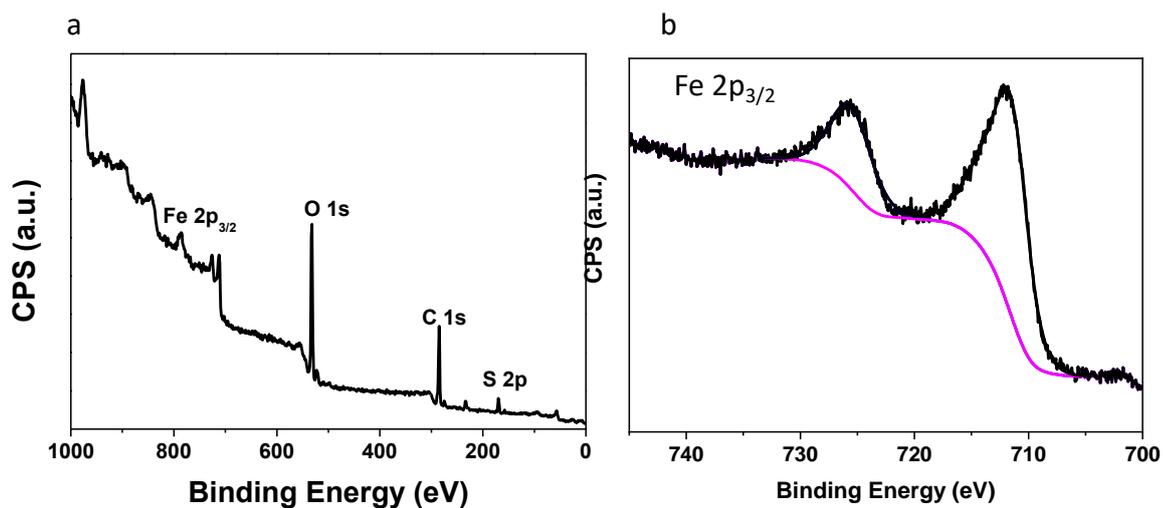


Figure 3

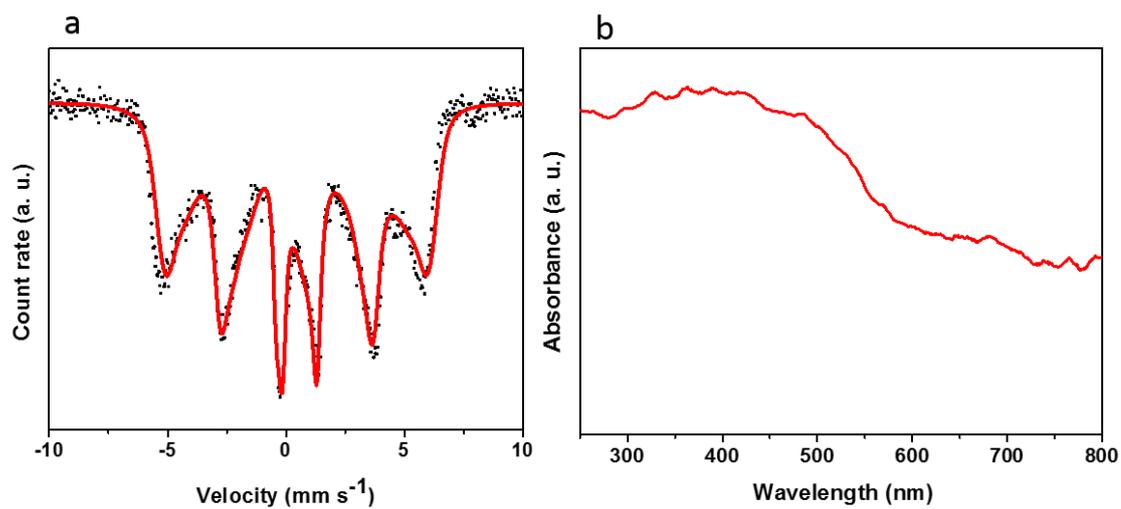


Figure 4

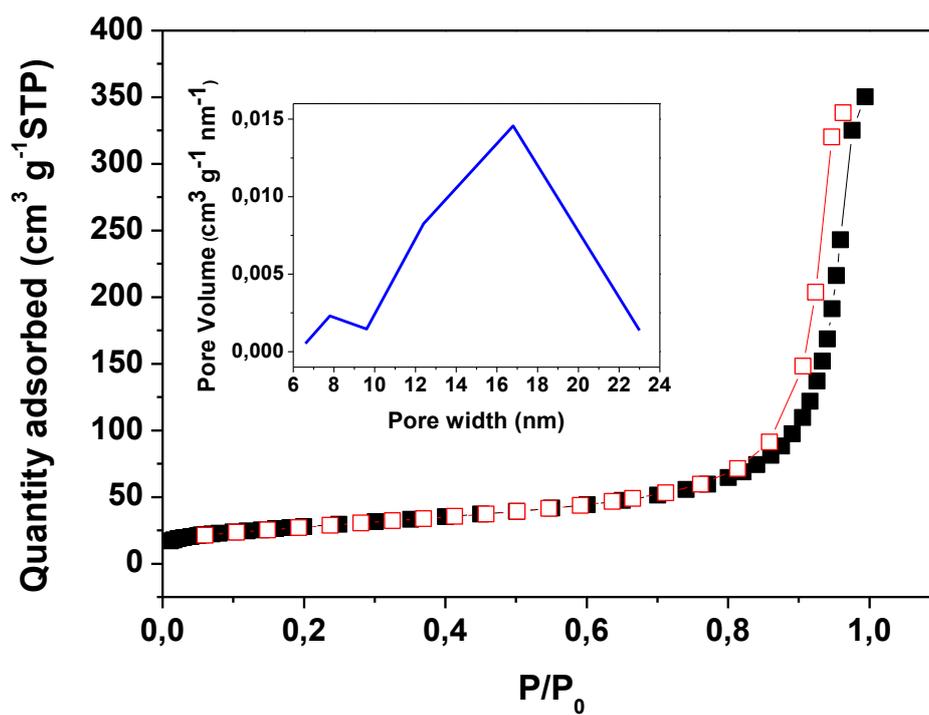


Figure 5

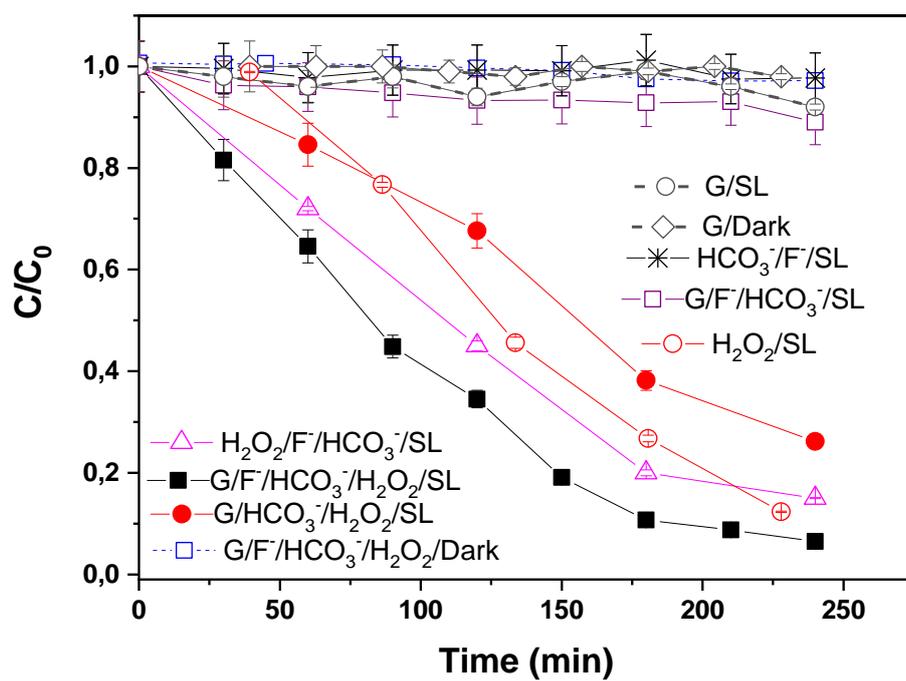


Figure 6

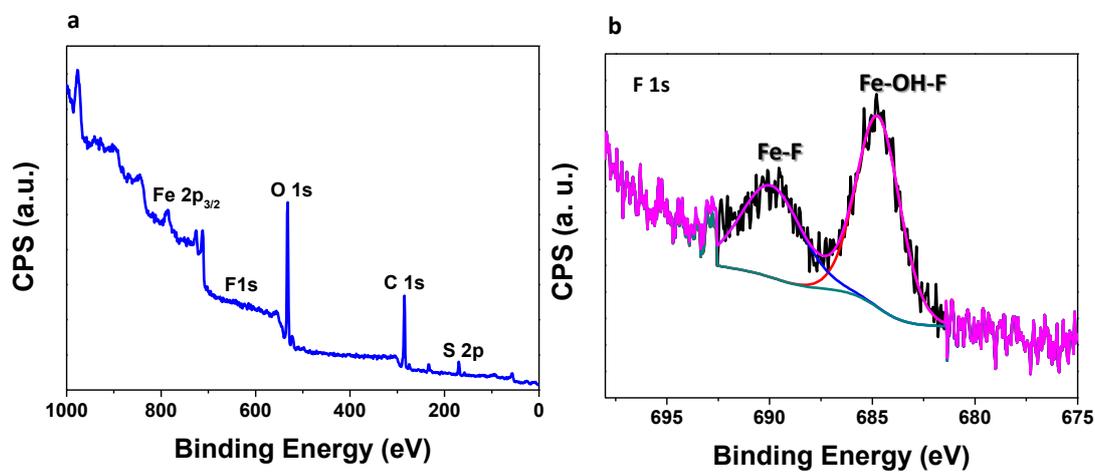


Figure 7

