

Goethite (α -FeOOH) photocatalytic activity at natural concentrations by the addition of H_2O_2 at neutral pH and the simultaneous presence of fluoride and bicarbonate.

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Abstract

The effect of the simultaneous presence of fluorine ($0.15\text{--}1.2\text{ mg L}^{-1}$), bicarbonates ($83.6\text{--}596\text{ mg L}^{-1}$), and synthesized goethite (0.3 mg L^{-1}) at typical concentrations often found in natural 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^{-2}) and H_2O_2 concentrations of 10 mg L^{-1} . 2,4-D removal was strongly enhanced by the presence of fluoride. F^- could modify the surface of iron (hydr)oxide leading to the formation of surficial Fe-F bonds benefiting the formation of free $^*\text{OH}$ radicals, producing upward band bending, reducing the electron-hole recombination, and enhancing the electron transfer to H_2O_2 . On the other hand, bicarbonate may react with $^*\text{OH}$ radicals generating CO_3^{*-} species which could be able to participate in pollutant oxidation as well while solar light-induced H_2O_2 photolysis also played an important role in removing 2,4-D. These findings suggest that “natural” tuning of iron (hydr)oxides by fluoride could take place in natural groundwater generating “natural” photocatalysts with a high activity which could participate, by adding H_2O_2 , in the enhancing of sunlight photoinduced natural abiotic processes to pollutants abatement.

1. Introduction

Geochemical processes occurring in natural groundwater grant to these samples interesting physical-chemical features such as the presence of bicarbonate, fluorine, and colloidal iron, the latter in form of (hydr)oxides as goethite (α -FeOOH) and lepidocrocite (γ -Fe-OOH). Natural 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 ($^*\text{OH}$) ($E^\circ = 2.7\text{ V vs. NHE}$) which would be responsible for organic pollutants removal in sunlight irradiated surface and well waters. However, the concentration of solar light photoinduced $^*\text{OH}$ radicals in surface waters is low ($\sim 10^{-17}\text{ mol L}^{-1}$), so their effect on the degradation of contaminants would be negligible. For this reason, it is necessary finding strategies to enhance natural abiotic photoinduced processes in waters aiming to the removal of chemical and microbiological pollution, thus, altering as little as possible the water environment. The addition of hydrogen peroxide (H_2O_2) to natural groundwater samples has been explored for our group exhibiting a promising result to achieve the bacteria inactivation and the removal of organic pollutants.

Goethite is a visible light-absorbing iron (hydr)oxide with apparent promising photocatalytic activity removing both bacteria and organic pollutants from water . 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) avoiding an efficient electron transfer and increasing thus charge carriers recombination .

Interestingly, Du et al., 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⁻¹ were strongly enhanced by the presence of fluorine amounts ranging between 8.5-85 mg L⁻¹. 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) degradation and bacteria inactivation in natural well waters by the addition of H₂O₂ (10 mg L⁻¹) under simulated sunlight irradiation was strongly enhanced by the presence of natural amounts of fluoride (0.1-1.2 mg L⁻¹) . Since fluoride and goethite are often found in groundwater samples, their mutual contact in these waters may induce “natural” fine-tuning leading to the generation of “natural” fluoridated iron (hydr)oxides with probably enhanced photocatalytic activities. In addition, the natural presence of other anions in these waters such as bicarbonates may have an important effect since these can react with *OH radicals yielding a less oxidative carbonate radical (CO₃^{-*}) (Edeg= 1.78 V vs NHE) would be also able to participate in the degradation of organic pollutants . These outcomings demonstrate that the chemical matrix of groundwater could exert an important role in the removal of organic pollutants or bacteria from natural waters photo-induced by goethite/H₂O₂ system or pristine goethite.

In this sense, photo-induced removal of 2,4-D by goethite (α-FeOOH) at natural concentrations found in well waters (0.3 mg L⁻¹) by addition of H₂O₂ at neutral pH and simultaneous presence of fluoride and bicarbonate, in natural amounts, was evaluated. These results would demonstrate that only the addition of hydrogen peroxide would be necessary to carry out photo-Fenton-like and photocatalytic processes for effective removal of organic contaminants in natural waters with the presence of these species and how fluoride and bicarbonate ions would affect its performance. This fact may avoid the use of iron salts, photocatalysts or complexing agents in natural groundwater samples as commonly reported. The effect of the fluoride and bicarbonates concentrations often found in groundwater samples on 2,4-D removal at pH 6.9 under simulated sunlight irradiation and simultaneous presence of H₂O₂ and goethite was carried out by using a response surface model (RSM) of type screening factorial design 2².

2 Experimental Section

2.1 Chemicals

All chemicals, including Ferrous sulfate (FeSO₄·7H₂O, Carlo Erba), sodium hydroxide (NaOH, Carlo Erba), acetonitrile (Sigma-Aldrich), 2,4-dichlorophenoxyacetic acid (2,4-D, Sigma-Aldrich), hydrogen peroxide (H₂O₂, Carlo Erba), Sodium fluoride (NaF, Sigma-Aldrich), sodium bicarbonate (NaHCO₃, Sigma-Aldrich) and Milli-Q 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., with some changes. In resume, 5.5 g of FeSO₄·7H₂O were dissolved in 100 mL of distilled water. The solution pH was adjusted to 7.0 by the addition of NaOH (1.0 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 ⁵⁷CoRh source.

Spectrometer was calibrated using a 12 μm thick pure Fe foil. X-ray photoelectron spectroscopy (XPS) analyses were carried out with XPS Analyzer Kratos model Axis Ultra with a monochromatic $\text{AlK}\alpha$ and charge neutralizer; diffuse reflectance spectroscopy (DRS) samples were recorded using a UV-vis Lambda 35, Perkin-Elmer spectrophotometer equipped with a diffuse reflectance chamber Labsphere RSA-PE-20, 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) 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^{-1} (0.2 mg L^{-1} of total iron) of goethite and fluoride ($0.15\text{--}1.20\text{ mg L}^{-1}$) and bicarbonate ($83.6\text{--}596.0\text{ mg L}^{-1}$) concentrations typically found in natural well waters at initial pH 6.9; this solution was stirred overnight. Then, 10 mg L^{-1} of H_2O_2 and 30 mg L^{-1} 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^{-2}). 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 300–400 nm (UV-B 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 superior to 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^{-1} 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 concern emerging contaminants (CECs) in water, it was chosen to permit adequate detection by HPLC equipment available in the laboratory.

2.5 Determination of total iron by atomic absorption spectroscopy

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

2.6 Photoinduced degradation of 2,4-D in presence of goethite, fluoride, and bicarbonate at natural concentrations by H_2O_2 addition. Factorial experimental design ²²

The photoinduced experiments were carried out according to previous work reported by Gutiérrez-Zapata et al, and following the methodology described in section 2.4. A factorial experimental design ²² was used to study the significant influence of two experimental factors: (A) F^- and (B) HCO_3^- concentrations, evaluated in two levels low (-) and high (+) which are often found in natural well waters on the degradation of 2,4-D pesticide in presence of natural goethite concentrations (0.3 mg L^{-1} ; 0.2 mg L^{-1} of total iron) and H_2O_2 (10 mg L^{-1}) at pH 6.9. The experimental matrix is presented in table 1 and additionally, control experiments such as dark reactions (Fenton), 2,4-D photolysis, and sunlight H_2O_2 -photolysis were also performed. Results were analyzed by using variance analysis (ANOVA) and response surface plots obtained by STATGRAPHICS centurion XVI Software.

3 Results and Discussion

3.1 Goethite physical-chemical characterization

Goethite was synthesized in the laboratory to be used as simulating the iron (hydr)oxide present naturally in groundwater and being characterized by several techniques to confirm its structure. XRD diffractogram of synthesized goethite (Figure 1a) exhibited peaks at 21.22° , 33.16° , 34.71° , 36.67° , 41.27° , 53.29° , and 59.09° ascribed to the presence of $\alpha\text{-FeOOH}$ (JCPDS-29-0713).

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

Observing the XPS survey spectrum (Figure 2a), it was evidenced the presence of signals attributed to Fe 2p, C 1s (due to adventitious carbon), O 1s, and S 2p (coming from residual FeSO₄) while the high-resolution spectrum of Fe 2p (Figure 2b) exhibited two signals at 711.6 and 725.8 eV often assigned to Fe³⁺ 2p_{3/2} and Fe³⁺ 2p_{1/2} in goethite [27–29].

Mössbauer measurements (Figure 3a) showed an asymmetric sextet with broadened lines, a hyperfine magnetic field (B_{hf}) around 33 T, and a quadrupole splitting (QS) of 0.45 mm s⁻¹ matching very well with goethite structure. Broadened lines and asymmetry could be related to poor crystallinity as it was confirmed by XRD diffractograms and the presence of Fe(II) respectively, the latter coming from synthesis precursor FeSO₄. DRS spectrum revealed a broad UV-vis light absorption comprised between 300-700 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 through a band gap energy of 2.7 eV [31].

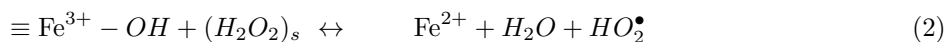
N₂ adsorption-desorption isotherms showed a typical type IV isotherm with hysteresis cycle H-3 corresponding to mesoporous materials according to the IUPAC convention, an average pore width around 16 nm (Figure 4) and BET-specific surface area of 98.31 m² g⁻¹. Similar textural features have also been reported for goethite.

3.2 Degradation of 2,4-D photoinduced by H₂O₂/goethite system in presence of fluoride and bicarbonates at natural concentrations.

Fenton-like, photo-Fenton-like, and photocatalytic processes were carried out with concentrations of goethite (α -FeOOH) often found in natural well waters (0.3 mg L⁻¹) in presence of H₂O₂ (10 mg L⁻¹), and the effect of natural concentrations of fluoride (1.2 mg L⁻¹) and bicarbonate (86 mg L⁻¹) was evaluated (Figure 5).

2,4-D at concentrations of 30 mg L⁻¹ did not undergo degradation in water containing HCO₃⁻ (86 mg L⁻¹) and F⁻ (1.2 mg L⁻¹) by simulated sunlight irradiation (Figure 5: HCO₃⁻/F⁻/SL), such as we have already reported under UV-B, UV-A, 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 claimed that heterogeneous Fenton reaction could take place in goethite/H₂O₂ systems yielding hydroxyl (*OH) and peroxy (HO₂*) radicals, the former able to oxidize organic molecules ($E^\circ = 2.31$ V vs. NHE) and the latter with a lower oxidizing power, dark experiments showed here that in presence of goethite (0.3 mg L⁻¹/0.2 mg L⁻¹ of total iron), H₂O₂ (10 mg L⁻¹) and anions (F⁻ and HCO₃⁻), 2,4-D concentration was not reduced (Figure 5: G/F⁻/HCO₃⁻/H₂O₂/Dark, being G: goethite). In the aforementioned report, authors suggested that, in dark conditions, H₂O₂ could be adsorbed onto goethite surfaces and undergoes further decomposition yielding *OH and HO₂* radicals (Eq. 1-3) (heterogeneous Fenton). Low concentrations of goethite used herein would be responsible for the minor role played by heterogeneous Fenton. Moreover, the dark adsorption of 2,4-D on goethite (G/Dark) was found to be negligible.

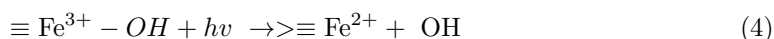


Photocatalytic reactions under sunlight irradiation (in absence of H₂O₂) of goethite in the presence or absence of anions led to a 2,4-D degradation of 10% after 240 min (Figure 5: G/SL; G/F⁻/HCO₃⁻/SL). As it was described above, α -FeOOH does not show an important photocatalytic behavior since its conduction band potential is very positive and unable to reduce molecular oxygen leading to the high e⁻/h⁺ pair recombination

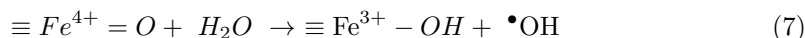
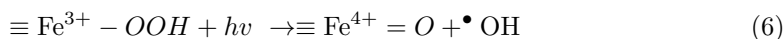
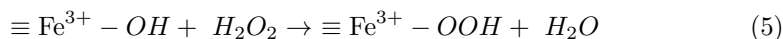
despite some authors have argued that goethite seems to be a promising photocatalyst removing several organic pollutants such as dyes, chlorophenols, and polycyclic aromatic hydrocarbons . However, in these aforementioned studies, goethite concentrations ranged from 1 to 500 g L⁻¹ (herein it was used a concentration of 0.0003 g L⁻¹) 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⁻¹ of H₂O₂ was added into 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/HCO₃⁻/H₂O₂/SL). Several authors have claimed the positive effect of H₂O₂ addition into α-FeOOH photocatalytic systems to degrade several pollutants . Nevertheless, these studies were performed by using α-FeOOH and H₂O₂ concentrations of 1 g L⁻¹ and 50-170 mg L⁻¹ respectively which are much higher than natural amounts of goethite (0.0003 g L⁻¹) and H₂O₂ (10 mg L⁻¹) used herein.

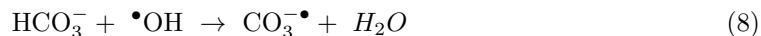
On the other hand, under sunlight irradiation, surface≡ Fe²⁺ species could be photoinduced (Eq.4) . These species could react with H₂O₂ leading to the generation of surficial ≡ Fe³⁺ and extra^{*}OH radicals (heterogeneous photo-Fenton) (Eq. 4).



Furthermore, surficial ≡ Fe³⁺ - OOH species generated by H₂O₂ adsorption on goethite surface could (Eq. 5), by UV-vis light irradiation, to photo-induce ferryl species (≡ Fe⁴⁺ = O), this latter very unstable in aqueous solutions, also leading to the formation of^{*}OH radicals (Eq. 7) .



Bicarbonates (83.6 mg L⁻¹) which were also present at typical concentrations often found in natural waters regulating the pH at 6.9, could react with ^{*}OH radicals generating carbonate radicals (CO₃^{-*}) (Eq. 8) able to remove 2,4-D as well . CO₃^{-*} radicals could participate in electron transfer and H-abstraction reactions leading to the oxidation of organic molecules . All these routes mentioned above could be responsible for the significant removal of 2,4-D in presence of bicarbonate.

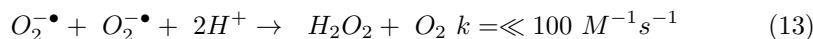
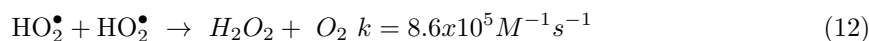


Surprisingly, experiments, where only hydrogen peroxide, fluoride, and bicarbonate were present (in absence of goethite) at concentrations of 10, 83.6, and 1.2 mg L⁻¹ respectively under simulated sunlight irradiation at initial pH 6.9, exhibited a strong 2,4-D removal of around 85% after 240 min (Figure 5: H₂O₂/F⁻/HCO₃⁻/SL). As it has been suggested, sunlight or UV-B light irradiation can photo-induce H₂O₂ photolysis (Eq. 9) . Pyrex-glass reactors used can allow the transmission to a lesser extent of UV-B light coming from the solar simulator leading to the H₂O₂ photolysis.



The experiments of H_2O_2 photolysis without anions (H_2O_2/SL) revealed that 2,4-D degradation underwent a slight reduction. Perhaps, bicarbonate reaction with *OH radicals leading to the generation of CO_3^{*-} could be behind the observed enhancement (Eq. 8).

The photocatalytic experiment in absence of fluoride ($G/HCO_3^-/H_2O_2/SL$) showed evidence about goethite could affect the *OH radical production by H_2O_2 photolysis. Two phenomena could be responsible for this detrimental effect: (i) H_2O_2 oxidation (+1.06 V vs NHE) by photoinduced goethite valence band holes (VB oxidation potential: +2.3 V vs NHE) could also take place producing a low oxidant peroxy radical (HO_2^*) (Eq. 10; Figure 7) unable to oxidize 2,4-D. Peroxyl radical is in equilibrium with superoxide radical (O_2^{*-}) (Eq. 11) and its pK_a is around 4.8, so at pH higher than pK_a (pH during experiments increased from 6.9 to 7.5) superoxide radical will be the main specie in solution which undergoes a fast disproportion leading to the generation of H_2O_2 (Eq. 12-13) [43].



On the other hand, (ii) goethite exhibits an important UV light absorption (Figure 3b) generating possibly a screen effect and competing with H_2O_2 molecules by UV-B photons.

Another pathway for ROS generation could be H_2O_2 direct reduction by goethite CB photoinduced electrons. Since 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_2O_2 reduction by goethite CB photoinduced electrons takes place leading to the generation of hydroxyl radicals (eq. 14).



As was expected, when natural amounts of fluoride (1.2 mg L^{-1}) were added to water containing already bicarbonates (83.6 mg L^{-1}) in presence of goethite and H_2O_2 (10 mg L^{-1}), the 2,4-D degradation increased markedly reaching 95% in 240 min of simulated sunlight irradiation (Figure 5: $G/F^-/HCO_3^-/H_2O_2/SL$). XPS measurements of goethite separated from the aqueous solution after the reaction confirmed the presence of fluoride on 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.

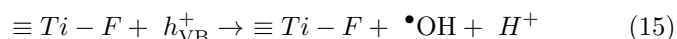
Hiemstra and Van Reimsdijk concluded that fluoride adsorption onto goethite is achieved on several surface sites being benefited at acidic pH values (goethite isoelectric point 7.9). Moreover, the authors suggested by theoretical calculations that the formation of surface Fe-F bonds would be feasible.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

As it was above mentioned, the beneficial effect of fluoride presence over photocatalytic degradation using goethite and lepidocrocite was first claimed by Du et al. . The use of $8.5\text{-}85 \text{ mg L}^{-1}$ fluoride increased the photocatalytic degradation of orange II dye at pH 6.5 by irradiation of these iron (hydr)oxides (0.5 g L^{-1}). Authors suggested that fluoride could modify the surface of iron (hydr)oxides increasing the production of *OH radicals, however, the mechanism was not proposed. Meanwhile, on TiO_2 a mechanism was suggested. In the literature there are several studies suggesting different mechanisms about how fluoride anions could enhance the photocatalytic activity of metal oxide semiconductors as TiO_2 . For instance, Minella et al., suggested that the flat band potential of semiconductors may be fine-tuned by surficial anion adsorption.

This flat band modification will depend on the nature and density of ions. Otherwise, Minero et al. , indicated that fluoridation of TiO₂ could enhance the photocatalytic activity of the metallic oxide towards the phenol degradation due to the formation of Ti-F surface sites. Authors suggested that the exchange of surficial -OH groups by F atoms on TiO₂ 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.

In addition, a systematic study reported by Deskins and coworkers where DFT calculations were carried out, demonstrated that rutile TiO₂ surfaces could be strongly modified by adsorbates (especially those molecules highly electronegative) tailoring the surface chemistry. Later, Montoya and Salvador measured the flat band potential of fluorine-modified TiO₂ finding that this underwent a negative shifting of about 80 mV compatible with upward band bending in semiconductors by an excess of negative charge in the surface. For their part, Xu et al. proposed a new theory where they suggested that fluoride ions present in the Helmholtz layer can induce the desorption of surface-bound ^{*}OH radicals photoinduced in TiO₂ surfaces through a fluorine hydrogen bond (Figure 6). This latter could support our results where the presence of two different species of fluoride interacting with the goethite surface were found by XPS.

Other authors have also suggested that the presence of surficial $\equiv Ti - F$ species may play an important role since photoinduced VB holes may be unable to oxidize the F⁻ ($E^*(F^*/F^-)=3.6$ V vs NHE) and would react directly with water molecules yielding free ^{*}OH radicals .



Thus, it is possible suggesting that α -FeOOH surfaces in presence of fluoride (at natural concentrations) can be superficially modified leading to either/both upward band bending or/and enhanced generation of free hydroxyl radicals upon sunlight irradiation (Figure 7). Upward band bending could enhance the H₂O₂ reduction by photo-induced conduction band electrons in goethite (Eq. 14) yielding more efficiently ^{*}OH radicals, therefore, enhanced photocatalytic degradation of 2,4-D, such as was observed.

The effect of homogeneous photo-Fenton reactions was also assessed since often iron (hydr)oxides can undergo photoinduced iron dissolution in water . Factors such as acidic pH and the presence of aliphatic acids as oxalate (by forming soluble ferric-oxalate complexes at circumneutral pH, for this reason, herein photocatalytic experiments were not carried out in absence of bicarbonates, since under these conditions, the pH of the solution dropped reaching values about of 4.0 promoting goethite dissolution) can also enhance iron dissolution. The presence of dissolved iron either complexed or not can induce homogeneous photo-Fenton reactions in presence of hydrogen peroxide . 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 μ m filtration after the photochemical and Fenton-like reactions. In dark experiments, the total iron concentration was 2.81 μ g L⁻¹ while the simulated sunlight-irradiated experiment in absence of hydrogen peroxide showed an iron concentration of 2.9 μ g L⁻¹. The simultaneous presence of goethite, anions (F⁻ and HCO₃⁻), H₂O₂, and simulated sunlight exhibited an iron concentration of 11 μ g L⁻¹. These iron amounts are too low to induce Fenton or photo-Fenton reactions at neutral pH able to generate appreciable concentrations of ^{*}OH radicals responsible for herbicide removal; pointing out that the degradation was mainly due to heterogeneous photo-Fenton processes/sunlight H₂O₂ 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 2² was used to study the effect of natural concentrations of fluoride (0.15-1.2 mg L⁻¹) and bicarbonates (83.6-596.0 mg L⁻¹) typically found in natural groundwater samples on simulated sunlight irradiated-goethite (0.3 mg L⁻¹; 0.2 mg L⁻¹ of total iron) degradation of 2,4-D (30 mg L⁻¹) in presence of 10 mg L⁻¹ of H₂O₂ at pH 6.9 after 90 min of sunlight irradiation. ANOVA results confirmed a polynomial equation of second order with R²=99.87 and P-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 mg L^{-1}) plays a significant role. Moreover, the combined interaction of bicarbonates and fluoride at their maximum levels (596.0 mg L^{-1} and 1.2 mg L^{-1} respectively) also exerted an important role in herbicide degradation. This was corroborated in Figure 8c where the factor interactions chart was shown, and it was observed that high bicarbonate and fluoride concentrations exhibited a high 2,4-D degradation.

Results suggest that fluoride and bicarbonate ranging at concentrations typically found in natural groundwater samples could have a positive effect on the 2,4-D removal using goethite at natural concentrations by adding H_2O_2 doses of 10 mg L^{-1} under simulated sunlight irradiation. This finding has important environmental implications since it should be probable that the simple addition of hydrogen peroxide onto natural groundwater samples upon natural sunlight irradiation may enhance several photo-induced phenomena implying natural fluorinated 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 natural groundwater samples could play an important role in sunlight photo-induced reactions in presence of H_2O_2 (10 mg L^{-1}) to the abatement of organic pollutants. We have suggested that goethite fluorination may take place leading to an increase of iron (hydr)oxide photocatalytic activity while the reaction between photoinduced $\cdot\text{OH}$ radicals and bicarbonate (HCO_3^-) could lead to the formation of carbonate radicals ($\text{CO}_3^{\cdot-}$) which may exhibit an interesting oxidizing power able to degrade 2,4-D molecules as well.

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

Acknowledgments

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References

Figure captions

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

Figure 2. Goethite XPS characterization. (a) XPS survey spectrum, (b) Fe $2p_{3/2}$ high-resolution spectrum.

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

Figure 4. N_2 adsorption-desorption profile of goethite. Insert indicates the pore volume and diameter distribution.

Figure 5. Photocatalytic degradation of 2,4-D (30 mg L^{-1}) under simulated sunlight irradiation (300 W m^{-2}) and dark conditions in Milli-Q water containing goethite (G) (0.3 mg L^{-1} (0.2 mg L^{-1} of total iron)), fluoride (1.2 mg L^{-1}), bicarbonate (86.3 mg L^{-1}) and H_2O_2 (10 mg L^{-1}) 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. XPS Fe $2p_{3/2}$ high-resolution spectrum of goethite in contact with fluoride (1.2 mg L^{-1}) 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 mg L⁻¹(0.2 mg L⁻¹ of total iron)) and H₂O₂ (10 mg L⁻¹) at initial pH 6.9 after 90 min of simulated sunlight irradiation (300 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 interactions chart. The final pH in all experiments was 7.5. The temperature was not higher than 38 °C.

Table captions

Table 1. Matrix of factorial experimental design.

Tables

Table 1

Factor	Levels	Levels
	Low (-)	High (+)
A: F ⁻ (mg L ⁻¹)	0.15	1.20
B: HCO ₃ ⁻ (mg L ⁻¹)	83.6	596.0
Run	Factors design	Factors design
	A	B
1	-	-
2	+	-
3	-	+
4	+	+

Figures

Figure 1

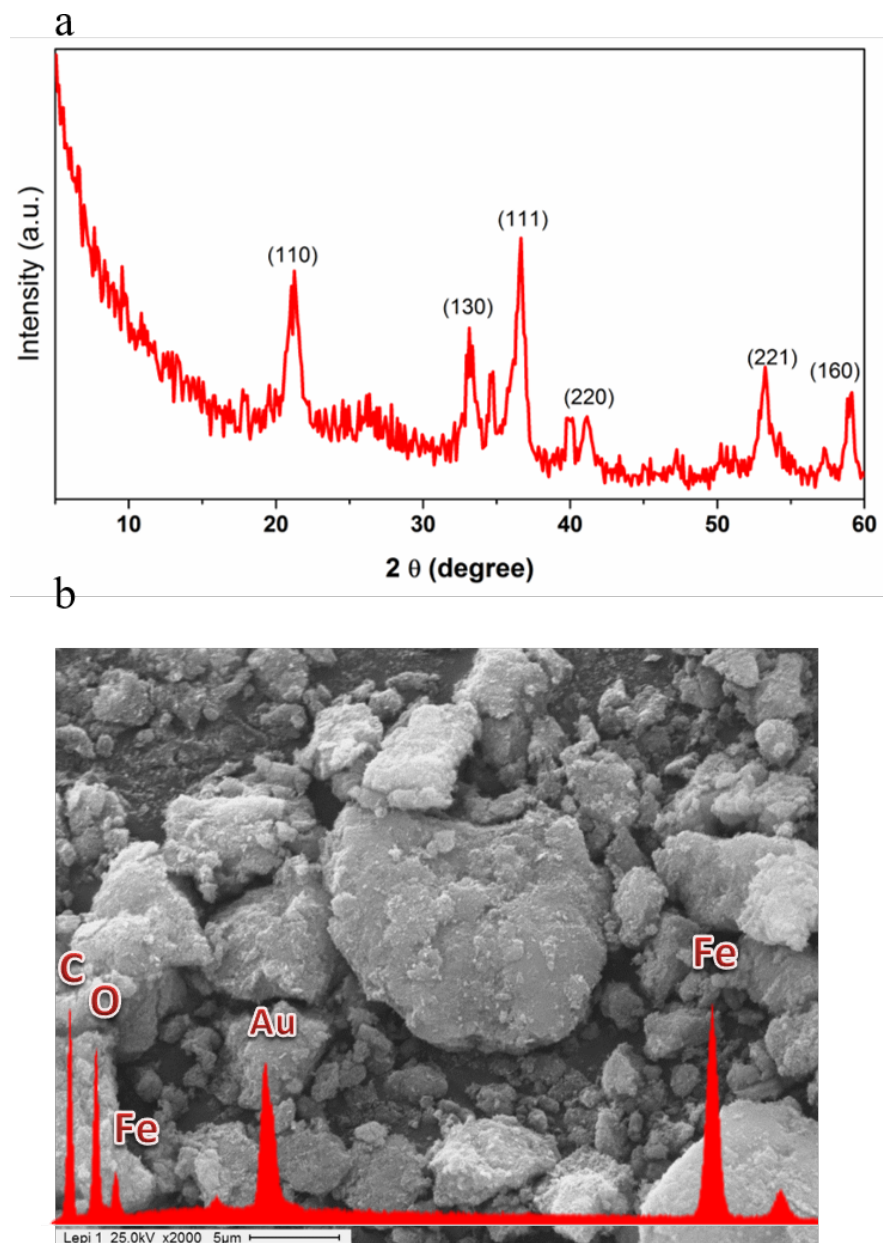


Figure 2

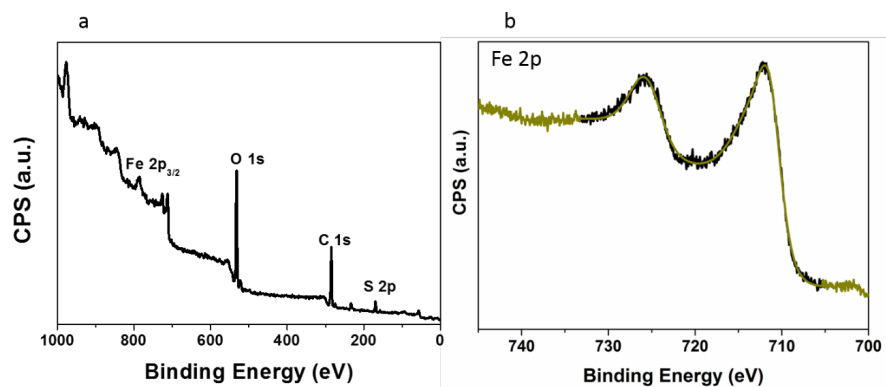


Figure 3

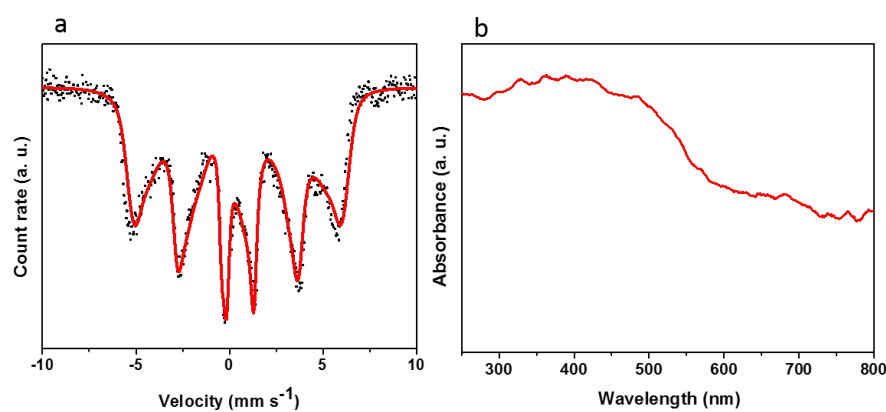


Figure 4

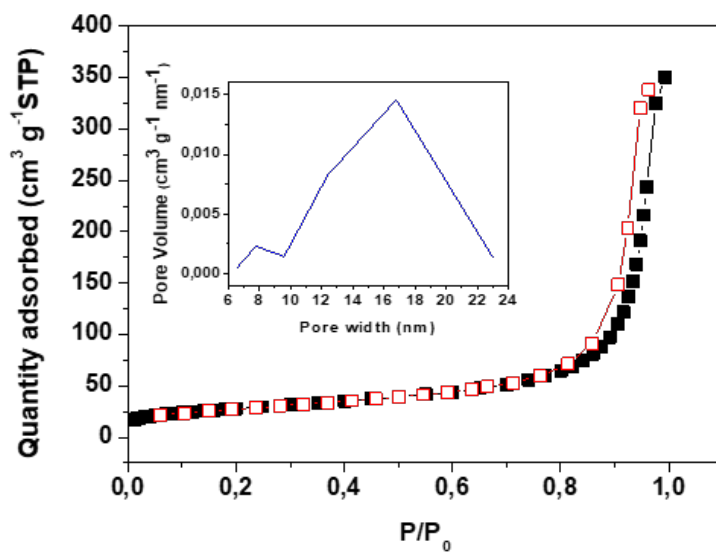


Figure 5

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Figure 6

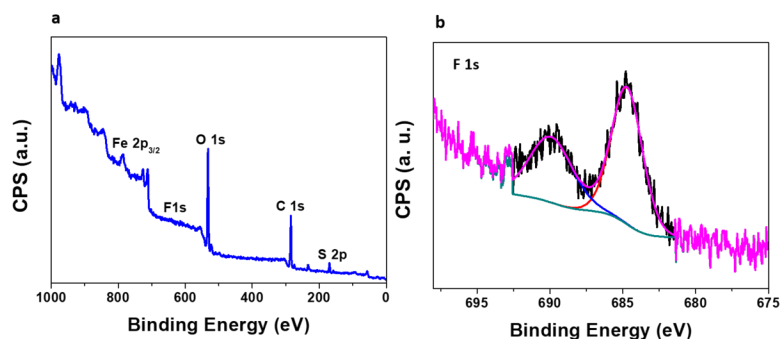


Figure 7

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Figure 8

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