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Additional Information

Strategies to Drive Photo-Fenton Process at Mild Conditions for the Removal of Xenobiotics from Aqueous Systems

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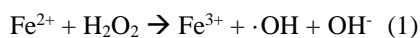
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Abstract: The aim of this paper is to provide an overview on the different approaches that can be employed to drive a photo-Fenton process under mild conditions, using both heterogeneous and homogeneous iron sources. For this purpose, sections are devoted to the following strategies: a) addition of iron at low concentrations; b) using the matrix of the effluent in order to avoid deactivation of iron; c) addition of chemical auxiliaries to form photoactive complexes with iron, such as carboxylates, chelating agents and humic-like macromolecules; d) strategies leading to the application of heterogeneous photo-Fenton process, by using iron-based solid particles or by hosting iron on different supports and; e) using heterogeneous iron sources as a reservoir for constant dosing of homogeneous iron photocatalyst. In particular, the review will focus on the elimination of emerging pollutants (e.g. drugs, personal care products or pesticides at low concentrations) which are the effluents where applying neutral photo-Fenton seems especially meaningful, although relevant works with other families of pollutants are also considered.

Keywords: wastewater treatment, photo-Fenton, mild pH, complexing agents, heterogeneous process, xenobiotics.

1. INTRODUCTION

Photo-Fenton can be found among the most promising photochemical advanced oxidation processes that has been employed for the removal of organic pollutants. It is based on the Fenton reagent, which consists in a mixture of iron salts and hydrogen peroxide, in which iron behaves as a catalyst to decompose hydrogen peroxide into highly oxidizing species, such as hydroxyl radical (OH). The reaction is greatly enhanced by UV-visible irradiation ($\lambda < 500$ nm). Although the mechanism is still under discussion, there is an agreement that the key reactions are described by equations 1-2 [1]. However, the involvement of other reactive species, such as highly oxidized iron species (e.g. ferryl cation) cannot be ruled out and may play an important role at some experimental conditions.



The effect of light can be understood, as equation (2) requires irradiation. For this reason $\text{Fe}(\text{OH})^{2+}$, the species that suffers photolysis is key in photo-Fenton. It is well established that $\text{Fe}(\text{OH})^{2+}$ reaches its highest concentration at a pH of ca. 2.8, which has been reported as the optimum pH for photo-Fenton [2]. This highly acidic pH represents a major drawback for the economic viability of this process, as costs related with pH modification (in most cases acidification followed by neutralization before discharge) are significant [3].

This is especially true when applying photo-Fenton to deal with effluents containing pollutants of high concern but present at low concentrations, such as the emerging pollutants. In fact, there is recent literature on the use of photo-Fenton for this purpose (e.g. pharmaceuticals, personal care products or effluents of wastewater treatments plants). Due to the low concentration of these xenobiotics (typically $\mu\text{g/L}$ or even ng/L), the reaction time is expected to be short and a certain loss of efficiency of the process could be acceptable if pH modification can be avoided or minimized.

Different strategies have been tested in recent years to apply photo-Fenton at mild conditions. In general, they can be classified in two wide groups, namely those trying to keep photochemically active iron species in solution at mild pH and those adding heterogeneous iron sources (although solubilized iron is partly or completely responsible for the reaction). Within the first group can be found: a) using iron at low concentrations, b) taking advantage of the matrix of the effluent and c) addition of complexing agents. The approaches involving heterogeneous iron sources can be divided in d) those strategies trying to apply, at least partly, an heterogeneous photo-Fenton process and e) using the heterogeneous iron as a reservoir for constant dosing of homogeneous iron photocatalyst.

With this background, the aim of this review is to report on recent research devoted to the application of neutral or mild acidic photo-Fenton to treat xenobiotics following any of the five approaches above mentioned; rather than an exhaustive

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literature survey, significant examples on each approach are provided and discussed.

Finally, other processes related to photo-Fenton have also been studied at circumneutral pH. One possibility is to substitute iron by other cation, such as copper, aluminum, chromium or cobalt to drive a photo-Fenton like process, as recently reviewed by Bokare and Choi [4]; also photo-electro-Fenton has been used for this purpose, as recently reviewed [5]. However, we think that they fall out of the scope of this work, as also happens with the use of mild photo-Fenton for disinfection [6,7].

2. PHOTO-FENTON WITH IRON AT LOW CONCENTRATIONS

As indicated in the previous section, formation of iron oxides or hydroxides, unable to drive a photo-Fenton process, represents the major hindrance to extend this treatment to milder pH values. According to Figure 1, the solubility of Fe(III) decreases with pH, as the predominant species varies from highly soluble Fe^{3+} to the very insoluble $\text{Fe}(\text{OH})_3$. However, even at neutral pH a small fraction of iron remains soluble, partly as $\text{Fe}(\text{OH})^{2+}$.

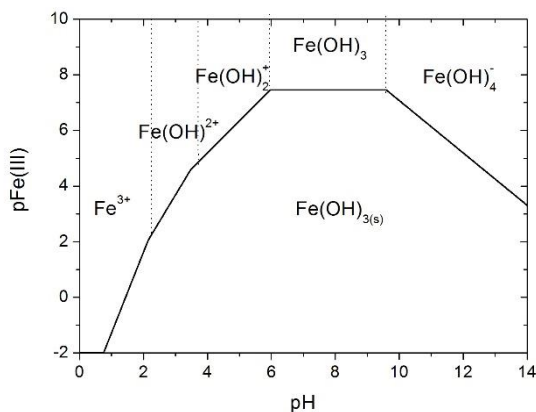


Figure 1: Iron speciation vs. pH and iron concentration.

One strategy that has been tested is to add iron at low concentrations (ca. 1 mg/L or even less) in order to be close to the amount of iron that is active at the working pH, thus minimizing the loss of iron by precipitation. This procedure might be meaningful to treat pollutants at trace concentrations, as even a low amount of catalyst might be able to generate a sufficient quantity of reactive species to remove the pollutants within an acceptable irradiation time. Some recent examples can be found in literature [8-17].

For instance, this approach has been employed to remove eight micropollutants in the presence of low concentrations of iron (μM). Irradiations were performed with UVC; however important degradations were also found in the absence of Fe, that could be associated to photolysis [9]. Furthermore, modification of pH throughout the process and generation of

carboxylic by-products may enhance the process. The role of carboxylic acids will be discussed in section 4; regarding to the pH modification, it is common that photo-Fenton results in an acidification of the solution and iron that was inactive at the initial pH could be increasingly activated when approaching to $\text{pH} = 3$. In fact, a limit for this homogeneous photo-Fenton has been established at $\text{pH} = 5.7$ for resorcinol degradation under solar irradiation [18]; that means that once solution reaches this value, the process is greatly accelerated.

Photo-Fenton has also been driven under solar irradiation with real effluents; Klammer et al showed that pollutants at trace amounts can be removed without pH modification using low concentrations of iron and hydrogen peroxide. However, it was necessary to decrease slightly the pH in order to remove bicarbonates from the solution. Interestingly, this study has been performed with a real effluent from a wastewater treatment plant, which has been spiked with different pollutants [17]. In this context, it is important to remark that when low amounts of iron are present, the matrix of the sample plays a very important role, and very different results have been obtained when working with tap or distilled water. In fact, some ions such as bicarbonate have been reported to be detrimental for the process, either by inducing changes in the coordination sphere of iron or by scavenging the formed reactive species. On the other hand, presence of organic matter may enhance the process, most probably because of its ability to complex iron.

Alternatively, some authors have tried to drive photo-Fenton at mild pH conditions by continuously adding iron in order to compensate for the loss due to precipitation. This procedure has been followed to remove a mixture of pesticides under solar irradiation, and rate constants close to those measured at acidic medium were reached. However, this methodology is limited by the higher amount of iron that is required and the difficult determination of the optimal sequence for iron addition [19].

3. USING THE MATRIX OF THE EFFLUENT

Some recent papers have shown that photo-Fenton can be applied at pH above 3 without important loss of efficiency or even shifting the optimum pH towards higher values. This is a very important issue that should be studied when dealing with a new type of effluent as, if acidification until pH close to 3 could be avoided, important economic and ecological advantages related with pH modification would be achieved. In particular, in samples containing phenols, the optimum pH was shifted to values close to four, most probably due to complexation of iron with the phenolic compounds [20]. This might be an important point when dealing with phenols-rich effluents such as food processing wastewaters.

Another interesting example is the removal of natural organic matter in a tertiary treatment for drinking water. These substances generate disinfection by products, and hence, they have to be removed before chlorination. When applying solar photo-Fenton as a tertiary treatment with low concentrations

of iron, very similar efficiencies were found in the range of pH between 3 and 7. In particular, good results were reached with 1 mg/L of iron at pH = 5 [21]. Another work also demonstrated that, under simulated sunlight, removal of humic acids by photo-Fenton was very efficient until pH close to 4, and noticeable reaction was observed throughout the studied pH range [22]. These results might be attributed to the ability of humic substances to complex iron, as will be reported in next section. This effect might involve that effluents containing humic-like substances (e.g. landfill leachates) could be treated at higher pH values.

Another group of effluents that can be used is metal industry wastes. In some cases, other metals rather than iron have been employed, (e.g. copper). For instance, Santos-Juanes et al. [23] used metal finishing effluents containing high amounts of copper to remove the cyanide that was present; for this purpose hydrogen peroxide was added and solar photo-Fenton was driven at pH = 12. Also metallurgical slags have been employed as photo-Fenton-like photocatalyst; however these processes should be predominantly considered as “in situ” iron generation and will be studied in section 6.

Finally, in a very recent work, iron present in natural waters (0.3 mg/L) was employed to drive a photo-Fenton process at pH = 7 to remove the pesticide 2,4-dichlorophenoxyacetic acid under simulated sunlight. This experiment shows that iron present in natural effluents can be used to treat pollutants present in groundwater [24].

4. ADDITION OF COMPLEXING AGENTS

In section 3, the possibility of extending the pH range for photo-Fenton in some effluents has been attributed to the formation of complexes with species present in the matrix. Hence, addition of substances able to form photo-active complexes with iron is a logical step forward and this approach is receiving increasing attention. In general, molecules and macromolecules with carboxy and/or amino groups are good complexing agents for iron, thus preventing formation of iron hydroxides at neutral pH values. In some cases, they have been demonstrated to drive photo-Fenton-like process. Table 1 summarizes complexing agents that have been employed and their chemical structure, and Table 2 details some examples and conditions in which have been applied.

| COMPOUND | CHEMICAL STRUCTURE |
|----------|--------------------|
| OXALATE | |
| CITRATE | |

| | |
|--------------|--|
| TARTRATE | |
| D-GLUCONATE | |
| GLUTAMATE | |
| CATECHIN | |
| PENICILAMINE | |
| EDTA | |
| EDDS | |
| NTA | |
| DCBPY | |
| HUMIC ACIDS | |

Table 1: Chemical structures of iron complexing agents that have been employed in photo-Fenton process.

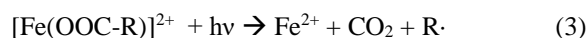
| Complexing agent | pH | Pollutant | Cites |
|------------------|----|-----------|-------|
|------------------|----|-----------|-------|

| | | | |
|---------------|-----------|--|----------|
| Oxalate | 5.0 | 2,4-Dichlorophenol | [25, 26] |
| | 3.5 – 6.5 | 3-amino-3-methylisoxazole | [27] |
| | 2.8 - 5 | textile wastewater | [28] |
| | 5 - 6 | diclofenac | [29] |
| | 3 - 7 | oxytetracycline | [30] |
| | 7 | sulfamethoxazole | [31] |
| | 5 | trimethoprim, sulfamethoxazole | [32] |
| | 6 - 7 | rhodamine B | [33] |
| Citrate | 2.8 - 5 | textile wastewater | [28] |
| | 6 - 7 | carbamazepine, fluomequine, ibuprofen, ofloxacin, sulfamethoxazole | [34] |
| | 3 - 7 | oxytetracycline | [30] |
| | 7 | sulfamethoxazole | [31] |
| | 5 | alachlor | [35] |
| | 2.5 – 7.5 | terbuthiuron | [36] |
| | 3.5 – 8.6 | atrazine | [37] |
| | 7 | acetaminophen | [38] |
| Tartrate | 7 | sulfamethoxazole | [31] |
| D-Gluconate | 3 - 7 | inderal | [39] |
| Catechin | 6 - 7 | rhodamine B | [33] |
| Penicillamine | 7 | crotamiton | [40] |
| EDTA | 7 | sulfamethoxazole | [31] |
| | 7 | crotamiton | [40] |
| | 7 | Methylene blue | [41] |
| EDDS | 3,5 - 6,5 | 3-amino-3-methylisoxazole | [27] |
| | 6 - 8 | phenol, bisphenol A, sulfamethoxazole, carbamazepine, pyrimethanil | [42] |
| | 6 | urban wastewater | [43] |
| | 6.8 | imidacloprid | [44] |
| | 2.8 - 5 | textile wastewater | [28] |
| | 6 - 7 | carbamazepine, fluomequine, ibuprofen, ofloxacin, sulfamethoxazole | [34] |
| | 7 | urban wastewater | [45] |
| | 6.2 | 2,2-bis-(4-hydroxyphenyl) propane | [46] |
| | 6,2 | synthetic mixture | [47] |
| | 7 | crotamiton | [40] |
| NTA | 7 | sulfamethoxazole | [31] |

| | | | |
|-------------|-------|---|---------|
| dcbpy | 7 | 2,4-DCP, Orange II | [48] |
| | 6 | 2,4-Dichlorophenol Orange 2 | [49] |
| Humic acids | 7 | urban wastewater | [45] |
| | 7 | acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid | [50] |
| | 3 - 7 | acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid | [51-53] |
| Humic like | 7 | Crystal violet | [54] |

Table 2: Examples of mild photo-Fenton driven in the presence of complexing agents; pH conditions and treated pollutants are given.

It is well known that iron carboxylates undergo, upon irradiation, ligand to metal charge transfer reaction [55], that enhances the reduction of iron, thus resulting in an acceleration photo-Fenton, in addition to iron stabilization [1, 56]. Furthermore, some of these compounds show stronger absorption band in the UVA-vis and higher quantum yields when compared with iron aquo-complexes. However, the mechanism involves decarboxylation of the ligand, as shown in equation 3, what results in a sacrificial role of the carboxylate that should be added, at least, in stoichiometric amount. Furthermore addition of extra amounts of organic matter to an effluent for detoxification should always be considered a drawback and this amount should be minimized [31, 57].



Oxalic acid is the carboxylic compound that has been more widely employed; its molecular weight is very low, and hence the amount of organics per mole is minimized and the by-products that are generated are not an important concern. Ferrioxalate has been employed to enhance photo-Fenton under simulated sunlight at pH = 5. Results were promising, even when scaled up to pilot plant. However high Fe:oxalate molar ratios (from 1:3 to 1:9) were used [29].

Alternatively, other carboxylic acids have also been used. In particular citric acid has been employed to degrade pesticides at several mildly acidic and neutral pHs [36, 37]. Also in this case, the mechanism involves a sacrificial role for citrate, as can be observed in Figure 2. Similar processes have been recently described for benzoic acid derivatives, which would help to explain the shifting in reactivity of effluents containing phenolic compounds, as described in the previous section. These species are able to photo-reduce Fe(III), undergoing a ligand to metal charge transfer reaction that results in decarboxylation of the ligand. Although, aromatics are less efficient than aliphatic carboxylates, this mechanism

could help to understand the extension of efficient photo-Fenton domain in effluents rich in phenolic compounds, as described in the previous section [58]

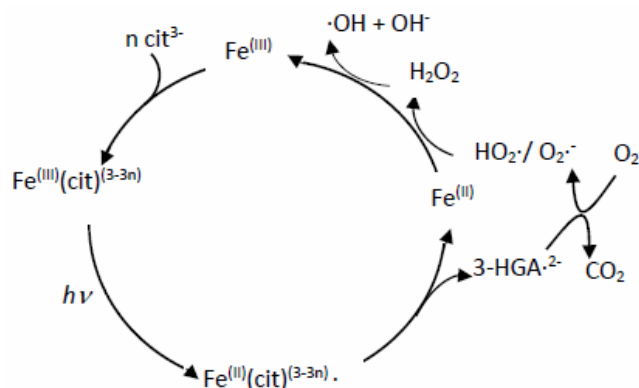


Figure 2: Scheme of the mechanism of the photo-Fenton process driven in the presence of citrate (cit^{3-}). Photoreduction of Fe(III) by citrate results in the formation of 3-hydroxylglutarate radical ($3\text{-HGA}\cdot^{2-}$). Extracted from [37]

Another group of substances used for iron complexation are bidentate chelating agents such as ethylenediaminetetraacetic acid (EDTA), ethylenediamine- N,N' -disuccinic acid (EDDS) or nitrilotriacetic acid (NTA). In particular, EDDS was proposed as an auxiliary for mild photo-Fenton by the research group of Mailhot et al. in 2012 [45], who observed that in the presence of this compound, the removal of bisphenol A, an endocrinal disruptor, could be achieved via photo-Fenton at neutral pH when irradiated with artificial UVA-vis light. Its performance was compared with other ligands, showing EDDS the best results (Figure 3)

EDDS has received increasing attention and it has been employed to treat deferent effluents and model compounds, using both, lamps and real sunlight. A detailed information on the pollutants that have been studied can be found in Table 2. Miralles et al. [43] investigated the removal of a mixture of pharmaceuticals at concentrations of a few $\mu\text{g/L}$ at neutral medium via photo-Fenton under solar irradiation. Citrate and EDDS were used as complexing agents. Both of them were able to enhance the oxidation process although high amount of those chemicals were required, as molar ratios Fe:citrate/EDDS were between 1:1 and 1:5. This resulted in an increase of the amount of hydrogen peroxide consumption. EDDS was also used to remove a set of 46 micropollutants from real and spiked wastewater treatment plant effluents. Results were very encouraging as the concentration of most pollutants quickly fell below the limit of quantitation. However, the process was strongly dependent on the sample matrix (in particular carbonates played an important inhibitory role), and the addition of EDDS resulted in an important increase (ca. 5 times) of the initial DOC [47]). In another paper, those authors compared the performance of photo-Fenton at $\text{pH} = 3$ and neutral pH in the presence of EDDS and humic acids; the target solution was the effluent of a wastewater treatment plant, containing emerging effluents

at ng/L concentration. Results indicated that 95% removal was reached in all conditions that were tested, although reaction was faster at $\text{pH} = 3$. However, neutral photo-Fenton with EDDS was indicated to be the most convenient, because of the low hydrogen peroxide consumption and the neutral pH conditions [45].

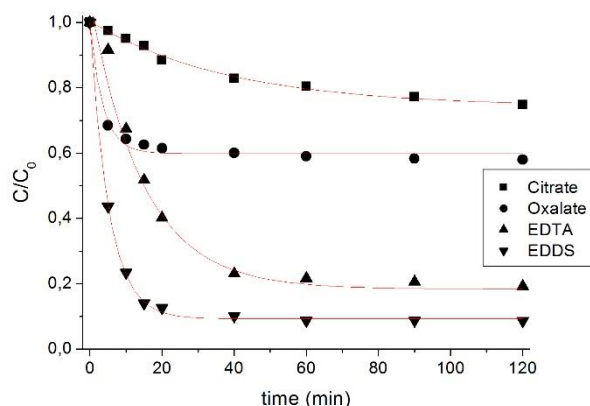


Figure 3: Effect of different iron(III) complexes on the degradation of bisphenol A at $\text{pH} = 6.2$.

NTA has been employed to treat sulfamethoxazole, a widely used antibiotic, at $\text{pH} = 7$ [34]. Its performance has been compared with other ligands, namely tartaric acid, oxalic acid and EDTA. As shown in Figure 4, best results were reached with EDTA and NTA, as higher percentages of antibiotic photodegradation has been reached with lower addition of organics that with tartaric acid and oxalic acid. However, authors the better biodegradability of NTA vs. EDTA makes the first one a better chemical auxiliary. Another work from the same research group has been devoted to study the stability of the Fe-NTA complex under the conditions of irradiation [59].

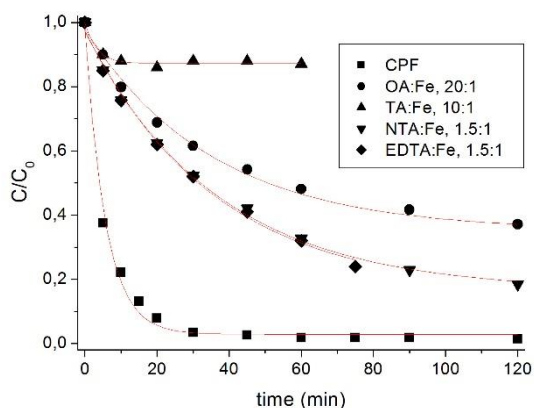


Figure 4: Sulfamethoxazole (0.079 mM) removal by photo-Fenton-like at neutral pH with Fe(III) chelates. In all cases $[\text{Fe}^{3+}]_0 = 0.089 \text{ mM}$ and $[\text{H}_2\text{O}_2]_0 = 0.294 \text{ mM}$. The studied conditions were: a) EDTA:Fe(III) = 1.5:1 (pH = 7.0 ± 0.7), b) NTA:Fe(III) = 1.5:1 (pH = 7.0 ± 0.7), c) tartaric acid:Fe(III) = 10:1 (pH = 7.0 ± 0.15), d) oxalic acid:Fe(III) = 20:1 (pH = 7.0 ± 0.15) e) SMX removal by conventional photo-Fenton (CPF); pH = 2.7 ± 0.1). Extracted from [34]

Macromolecules can also be used as complexing agent. Because of its high molecular weight, they have a high number of active sites per molecule and, if they suffer oxidation, some of those groups might be destroyed, but they could be replaced by others newly formed; hence, these substances are expected to be more resistant towards oxidation and to avoid the loss of efficiency observed in the photo-Fenton process in smaller molecules.

Humic substances are good complexing agents for iron in the environment, and in fact, photo-Fenton-like process mediated by those complexes have been reported as an important pathway for the removal of xenobiotics in aquatic ecosystems [60]. Vermilyea and Volker demonstrated that natural sources of iron and humic substances are able to drive photo-Fenton process, although different mechanistic pathways are involved [61]. In fact, experiments with fulvic acids indicated that these substances had an important influence in the redox cycle of iron, able to photoreduce Fe(III) as carboxylates, in a reaction that is faster at pH = 5 [62]. Based on these results, some authors have studied the possibility of driving mimetic processes in the laboratory, showing that humic substances-iron-hydrogen peroxide are able to enhance photodegradation of pharmaceuticals and pesticides at pH = 7 under simulated sunlight [45, 50]. However, the process was still too slow to be applied in real situations.

Substances with similar characteristics as humic acids can be isolated from different sources, such as urban wastes [63]. They are obtained following a procedure that involves basic digestion of the composted waste, filtration to remove the insoluble fraction and a membrane process to concentrate the humic substances in the retentate, that are obtained upon

evaporation of the solvent. This assembly of macromolecules have been named as “soluble bio-organic” substances (SBO) or humic-like substances (HLS). As shown in Table 2, a series of papers has been published in recent years reporting on the ability of these substances to drive circumneutral photo-Fenton. Results were strongly dependent on the experimental conditions as opposite factors are involved, the most important of which are: a) an improved generation of reactive species via photo-Fenton, b) the screen effect due to the colour of SBO, c) a competitive effect SBO-pollutant for the reactive species and d) the surfactant properties of SBO. Experimental design methodology have demonstrated that the pH domain where photo-Fenton can be applied is extended to pH ca. 5, beyond this point, there is a noticeable loss of efficiency (See Figure 5). Optimal concentrations of SBO were typically 10–20 mg/L and a low concentration of iron is required (3–5 mg/L) [52].

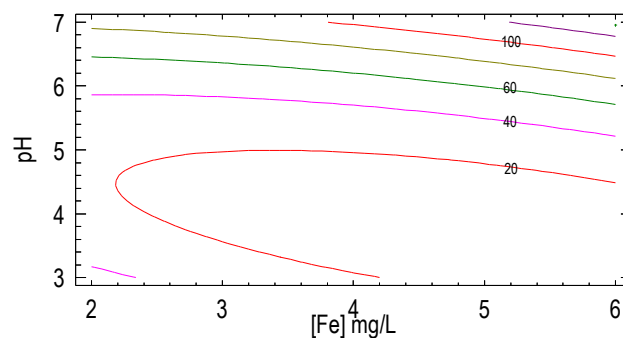


Figure 5: Contour plots for the time (min) the initial concentration of carbamazepine required to reduce to a 50% by a photo-Fenton process. The concentration of SBO was 25 mg/L and that of carbamazepine was 5 mg/L. Adapted from [52]

SBO are relatively stable towards chemical oxidation and no significant loss of efficiency can be observed along photo-Fenton. Different bioassays have demonstrated that those compounds are non-toxic and scarcely biodegradable [53]. Finally experiments have been driven with real sunlight at pH = 5.2.

5. PROCESS HETEROGENEIZATION

A very different strategy to drive photo-Fenton at neutral medium consists in using an active iron-containing solid surface, which can be iron-based minerals, iron coated particles or immobilized active iron species onto solid supports. Although this procedure has been mainly employed in Fenton processes, most probably due to scattering of light by the solid species, some examples can be found in literature on their application to photo-Fenton [64–92]. However, it has to be indicated that most papers are focused on the synthesis and characterization of the solid materials and they just provide one or two examples of their performance using model compounds.

A group of heterogeneous catalysts is composed by iron-containing minerals. Among them, iron oxides such as hematite, goethite or magnetite have been employed [64-71]. Figure 6 shows the rate constants determined for the removal of orange II in the presence of different oxides; interestingly, best results were reached with ferrihydrite, followed by maghemite which were the materials which produced higher pH decreases. Hence, pH might be important also in heterogeneous photo-Fenton; this could be due to iron leaching, more likely at lower pH, as indicated below. In some cases, these oxides are micro or nanoparticulated. In addition to this, hybrid oxides containing other metals have also been used. [72-77]. In this case, the leaching of toxic heavy metals constitutes a major concern.

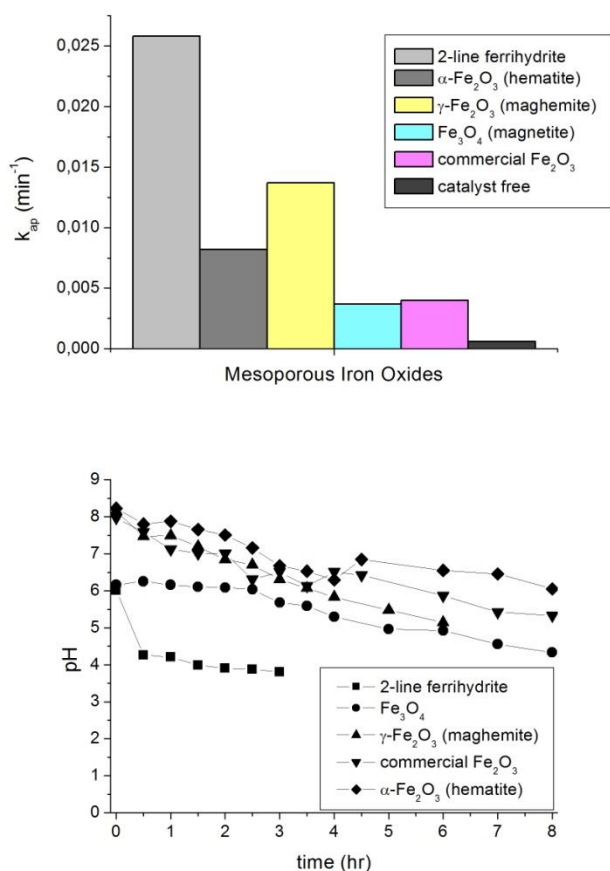


Figure 6: Above: Rate constants determined in the photo-Fenton decolorization of orange II in the presence of different iron minerals. Below: pH variation in the experiments. Adapted from [70].

Iron has been supported onto different materials such as zeolites [78-80], clays such as montmorillonite [81, 82], carbonous materials [83-86], membranes [87-89], resins [68], alginate [82] or silica [90]. Supporting iron onto adsorbents such as clays, zeolites or activated carbon seems meaningful in view of using photo-Fenton as a treatment for the regeneration of these materials. A similar strategy can be used with membranes, where photo-Fenton can be used to prevent fouling or to treat retentate.

Some hybrid materials have also been employed: for instance, an iron mineral, $\alpha\text{-FeOOH}$ has been supported onto an ion exchange resin, namely amberlite, to treat $17\beta\text{-estradiol}$ under UV irradiation. Although reaction was faster at $\text{pH} = 3$, photo-Fenton was still very efficient at pH as high as 11. Some iron leaching was observed, although concentration of iron in solution was systematically below 1 mg/L [68].

In fact, in some cases the real photo-Fenton process is attributable to a fraction of iron that remains in the solution. For instance, carboxylates are known to drive a photochemical process that solubilizes iron (III) present in heterogeneous or colloidal medium by means of a mechanism that involves reduction to soluble Fe(II) species [91]. Demarchis et al. when studying the removal of phenol by photo-Fenton in the presence of hematite as iron source observed leaching of small amounts of iron that might be responsible for the process via a homogeneous photo-Fenton [92]. However, this should not be considered as a major drawback from the practical point of view as the amount of iron present in the solution is commonly well below the limits set by legislation.

5. "IN SITU" GENERATION OF IRON

A possibility to overcome the inconvenience of iron inactivation at neutral medium is continuous release of active iron(II) or iron(III) species into the solution. As indicated in the previous section, solid iron-containing materials release iron cations into solution, which are able to drive photo-Fenton. Although in most papers researchers try to minimize this effect in order to drive heterogeneous photo-Fenton, in a few recent papers leaching of iron is favoured to drive homogeneous neutral photo-Fenton. However, as happened with heterogeneous processes, this strategy has been more widely applied in dark Fenton, because of the more difficult illumination of a solution containing solid particles [93-95].

The most widely employed strategy is the corrosion of zero valent iron (ZVI) [96]. However, recently, some authors have investigated to employ also the ability of ZVI to act as reductive agent. For this purpose, the process is driven with and without hydrogen peroxide. The reductive step is commonly employed to remove deactivating functional groups, namely nitroaromatics [97, 98]. Then, addition of hydrogen peroxide and irradiation (photo-Fenton step) is used to deal with the more easily oxidizable aminoaromatics. Figure 7 shows reduction of 4-nitrobenzoic acid by means of an iron wool to give 4-aminobenzoic acid; then, hydrogen peroxide was added and illumination began to drive a photo-Fenton with the iron released in the previous step.

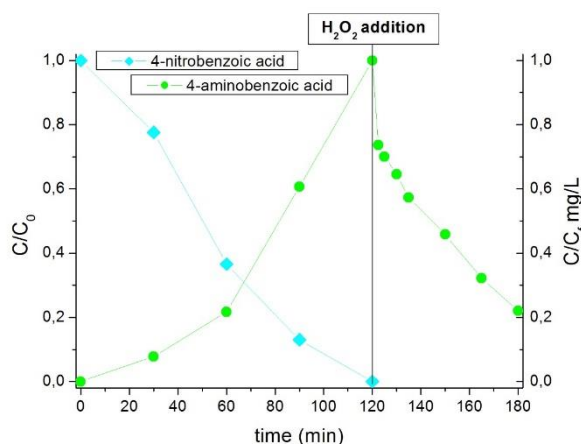


Figure 7: Plot of the relative concentration of 4-nitrobenzoic acid and 4-aminobenzoic acid along a combined process consisting a reductive phase (ZVI) followed by an oxidation (photo-Fenton) upon H_2O_2 addition. Taken from [97].

Also metallurgical slags have been employed as a source of photo-Fenton-like photocatalysts; Arzate Salgado et al., used copper and steels slags to treat diclofenac under simulated sunlight (Xenon lamp) at pH =7; although results did not improve dramatically the effect of hydrogen peroxide, most probably because the astringent pH conditions, some effect was observed. [99]. Other authors drive similar processes with other metals, such as copper, although again in thi case the toxicity of this heavy metal is a concern [100].

Iron minerals (e.g. goethite) can also be employed as a source of iron. Huang et al. published an interesting article in which combined this approach with the use of chelating agents. This system is highly dependent on reaction condition as opposite effects are found: surface inactivation by deposition of EDDS, which decreases heterogeneous photo-Fenton and enhancement of the homogeneous process because of iron stabilization by EDDS. As consequence, an optimum pH 0 6.7 was found for the degradation of bisphenol A with UVA-visible light (fluorescent tubes which irradiate in the 300-500 nm range) [69]

7. CONCLUSIONS

Shifting experimental conditions towards milder pH values is receiving increasing attention from researchers in the last decade. Different approaches have been used for this purpose, as indicated above, and each one seems meaningful for some niche application:

a) Using low concentrations of iron might be interesting to deal surfactants at trace amounts, such as xenobiotics at the effluents of wastewater treatment plants, as even inefficient generation of reactive species might be enough to remove those toxicants.

b) Investigation of the optimum pH when dealing with a new effluent is a meaningful task as it should not be taken for granted that a pH = 2.8 is the optimum for photo-Fenton. In fact, the presence of species able to complex iron could be rather common, and slight increases in working pH might represent significant savings.

c) The use of complexing agents is able to extend the range of application of photo-Fenton to pH values close to 5. This would allow the removal of target highly toxic pollutants, where addition of extra amounts of DOC is not a problem. Carboxylates or chelating agents such as EDDS or NTA have demonstrated to drive an efficient photo-Fenton. In this context, the use of non-toxic sustainable sources of complexing agents such as humic-(like) substances should be investigated, as they can be considered as a green process.

d) Heterogeneization of the process might be useful for some purposes, such as prevent fouling of membranes via supporting iron in their structure or regeneration of adsorbent materials. Iron containing nanoparticles could also allow using iron concentrations above the limits of discharge, recycling of the catalyst or an easy removal after the reaction. Although it is not a major drawback for application, solubilized iron might be responsible for the photo-Fenton process.

e) The use of elemental iron can employed to combine reducing with oxidizing steps, what is interesting to treat those compounds difficult to oxidize. Using other solid sources can be used to dose iron at low amounts, although this approach is limited by higher hydrogen peroxide requirements or scattering of light by the solid particles.

Nonetheless, much effort is still needed, on this issue. For instance, some of the approaches are very recent and hence their real applicability is not established yet, such as the ZVI/photo-Fenton coupling or determination of the optimum pH for photo-Fenton in complex effluents; in other cases, there are important drawbacks that should be overcome (for instance decreasing the amount of complexing agents, when they are employed, or stability of supported heterogeneized photocatalysts).

Furthermore most experiments have been carried out with model compounds at concentrations (mg/L) far above for those commonly found in those effluents that can be potentially treated, using distilled water as solvent; this is an important problem because the important effect of the matrix (e.g carbonates or dissolved organics) cannot be determined and significant parameters such as hydrogen peroxide amount or optimal complexing agent concentration cannot be determined. This might be due to the complex analytical tools required to monitor real systems.

Finally, mechanistic issues still remain uncertain. The complex manifold of equations involved in “classical” photo-Fenton becomes even more complex with the addition of new species or different experimental conditions that results in changes in the coordination sphere of iron. Hence alternative processes such ligand to metal charge transfer reaction, the involvement of excited states of organic molecules or the

presence of different oxidation of iron might result in the occurrence of new reaction pathways or the involvement of other reactive species rather than hydroxyl radical.

CONFLICT OF INTEREST

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