



Combining ZVI reduction with photo-Fenton process for the removal of persistent pollutants



L. Santos-Juanes^a, F.S. García Einschlag^b, A.M. Amat^a, A. Arques^{a,*}

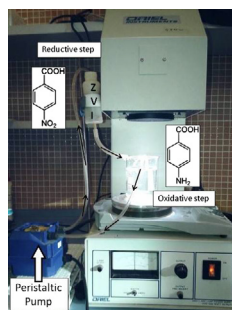
^aGrupo de Procesos de Oxidación Avanzada, Departamento de Ingeniería Textil y Papelera, Universitat Politècnica de València, Campus de Alcoy, Alcoy, Spain

^bInstituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA, UNLP, CCT La Plata-CONICET), Diag. 113 y 64, Sucursal 4, C.C. 16, B1906ZAA, La Plata, Argentina

HIGHLIGHTS

- An integrated process combining reductive and oxidative stages has been developed.
- Variation of experimental conditions allows favoring reductive or oxidative stages.
- This methodology might be useful to deal pollutants reluctant to oxidation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Available online 23 April 2016

Keywords:

Iron
ZVI
Photo-Fenton
Wastewater
Combined processes

ABSTRACT

An iron-based photochemical process able to act via reductive and oxidative stages by tuning experimental conditions has been explored. In a first step, zero-valent iron (ZVI), added as steel wool, was used to reduce those pollutants reluctant to oxidative processes. Then, the iron released in the solution was employed, upon addition of hydrogen peroxide, to drive a photo-Fenton process. This procedure has been checked with a mixture of five chemicals, namely p-toluenesulfonic acid, benzoic acid, p-nitrobenzoic acid, acetaminophen and caffeic. p-Nitrobenzoic acid resulted to be the most reluctant against oxidation but it was reduced in the absence of H₂O₂ to form 4-aminobenzoic acid; the presence of salts (e.g. tap water) was required and best results were reached at neutral pH. As p-aminobenzoic acid can be more easily oxidized than p-nitrobenzoic, combination of both stages is meaningful: a ZVI-based reduction followed by a photo-Fenton like-oxidation was employed to remove this pollutant from tested solutions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The photo-Fenton process is one of the most widely studied among the chemical oxidative methods for water treatment. It consists on a combination of ferrous salts and hydrogen peroxide at an optimum pH of 2.8, although reaction also occurs in the dark (dark Fenton or thermal Fenton), it is enhanced by UV-Visible irradiation, as the limiting reduction step of Fenton system becomes

faster when photo-induced [1,2]. The ability of this process to oxidize a wide range of pollutants under different experimental conditions is well established [3] and hence, increasing attention has been paid by researchers to photo-Fenton process during the last 20 years. Operational variables such as pH, effect of anions or cations, temperature, light sources, reactor design, process costs or automatization have been widely investigated [4–8].

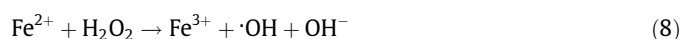
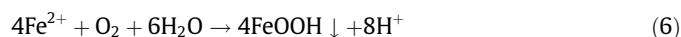
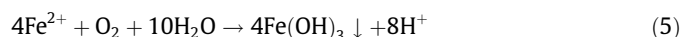
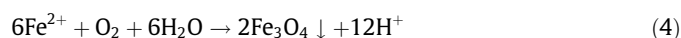
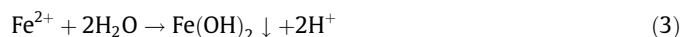
Despite the potential applications of this process, some compounds cannot be efficiently removed by photo-Fenton, either because of the formation of non-desirable by-products (e.g. chlorinated species [9]) or because of their low reactivity due to

* Corresponding author.

E-mail address: aarques@txp.upv.es (A. Arques).

the presence of electron-withdrawing groups (e.g. nitro groups, sulfonates, cyano group) that deactivate electrophilic attack of the reactive species [10]. These inconveniences can be overcome by either increasing reaction time or reagents concentrations (iron or hydrogen peroxide). Nevertheless, when the process is applied as tertiary treatment, the use of mild conditions (near neutral pH and low iron and hydrogen peroxide concentrations [11,12]), makes these approaches unattractive and therefore exploration of alternative processes is certainly necessary.

Among the alternative processes investigated, continuous release of iron to replace the amount that suffered precipitation has been studied to drive circumneutral photo-Fenton [13]. In this context, corrosion of zero-valent iron (ZVI) could be used as a continuous source of iron salts. When ZVI is present in water, the following reactions may occur [14]:



According to the reactions above, ferrous salts are released into the solution during the ZVI process. Once iron cations are present in solution, oxidizing reaction steps, based on (photo)-Fenton chemistry may also occur, in particular if hydrogen peroxide is added to the reaction mixture [15]. However, most of the studies using ZVI as source of iron cations for photo-Fenton involve the coexistence of zero-valent iron, the pollutant and H_2O_2 in the same reactor; under these conditions, inefficient consumption of hydrogen peroxide might occur, as corrosion of ZVI by H_2O_2 competes with key reaction steps of the photo-Fenton process. Furthermore, for photochemical processes, the use of solid substances in slurry or supported is disadvantageous as it results in light scattering, hence decreasing the amount of photons available for photochemical reactions. In this context, a process set up able to conduct ZVI corrosion and photo-Fenton stages in physically separated compartments seems meaningful.

It is worth to mention that, following the latter approach, the ability of ZVI to act as reducing agent (standard redox potential of -0.44 V) can also be employed; in fact ZVI-based processes are commonly employed for decontamination of water and groundwater [16,17]. In particular, ZVI has been used to remove different types of pollutants from water such as chlorinated compounds, arsenic, nitrate, dyes or nitro-aromatic compounds [18–20]. The reaction mechanism of contaminants reduction by ZVI is complex [21] and pH dependent. Furthermore, it has been reported that pH has a significant effect on the oxidation of more soluble Fe (II) species into highly insoluble Fe(III) [22].

In fact, photo-Fenton oxidative process and ZVI-based reduction could coexist, but according to the experimental conditions, one of them would be favored. For this reason, studying coupled process of reduction–oxidation would be meaningful for some niche applications, such as treatment of effluents containing pollutants reluctant to chemical oxidation [23]: a first ZVI-mediated stage could be applied to reductively modify substances reluctant to oxidation

into more labile by-products that will be in turn oxidized in a photo-Fenton based oxidative step. Furthermore, iron cations released by corrosion of ZVI could be employed in the photo-Fenton process.

With this background, the aim of this work is to study a combined ZVI-photo-Fenton process. Commercial steel wool has been used as an iron source and a reaction set-up able to separate ZVI-based reduction and photo-Fenton has been employed. As factors influencing the photo-Fenton process are well-known, special emphasis will be made on the reductive phase. For this purpose has been employed a mixture of five pollutants: p-toluenesulfonic acid and p-nitrobenzoic acid as examples of sulfonated and nitroaromatic compounds which are present in industrial effluents such as paper mill or textile dyes [24]; benzoic acid, used as preservative in cosmetics and pharmaceuticals and whose metabolites have some estrogenic effect [25]; and finally, acetaminophen and caffeine, which are systematically found in the effluents of wastewater treatment plants [26]. They are aromatic compounds bearing different functional groups (see Fig. 1 for structures), which results in different activation towards oxidative process, p-toluenesulfonic and p-nitrobenzoic acids being difficult to oxidize because of the presence of electron withdrawing groups directly attached to the aromatic ring, while the other three are more easily oxidized. The model mixture allowed us to comparatively evaluate not only the efficiency of each treatment stage (ZVI and photo-Fenton), but also the presence of antagonistic or synergistic effects in the combined treatment.

2. Experimental

2.1. Reagents

High purity acetaminophen, caffeine, benzoic acid, p-nitrobenzoic acid and p-toluenesulfonic acid were supplied by Sigma–Aldrich. Sulfuric acid (96%), ferrous sulfate (99%), hydrogen peroxide (30%) and acetonitrile (HPLC grade) were purchased by Panreac. The water matrices used were Milli-Q grade and tap water (pH = 7.4, inorganic carbon = 52 mg/L, conductivity = 510 $\mu\text{S}/\text{cm}$, $[\text{Cl}^-] = 27.8$ mg/L, $[\text{SO}_4^{2-}] = 33.3$ mg/L, water hardness = 142 mg/L of CaCO_3). The commercial steel wool can be classified as medium grade with a fiber thickness of ca. 0.06 mm. This product presents cylindrical form (6.5 cm long, 3.5 cm of diameter) and its weight was 6 g. A picture obtained by SEM is provided as [Supplementary information \(Fig. S1\)](#).

2.2. Chemical reactions

The experimental set-up employed in the combined ZVI-photo-Fenton process can be observed in Fig. 2. The steel wool was placed

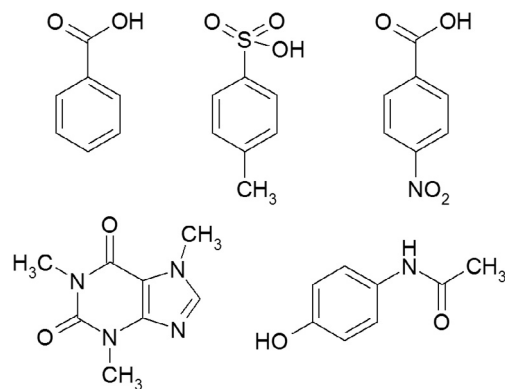


Fig. 1. Chemical structures of the pollutants used in this work; from left to right and from top to bottom: benzoic acid, p-toluenesulfonic acid, 4-nitrobenzoic acid, caffeine and acetaminophen.

into a cylindrical container placed over an open glass reactor with magnetic stirring. The solution was continuously recirculated from the open reactor to the steel wool at a flow rate of 20 mL/min using a peristaltic pump PR7 (SEKO). A solar simulator (Oriel Instruments, Model 81160 equipped with a 300 W xenon lamp) whose emission spectrum closely matches the solar one was employed to irradiate the open glass reactor. The apparatus was equipped with specific glass filters for cutting off the transmission of wavelengths below 300 nm was used. The UVA irradiance (320–400 nm) was 32 W/m².

The target solution consisted in a mixture of the five pollutants at an initial concentration of 5 mg/L each, the initial DOC concentration being 19.5 mg/L. For each experiment, the reactor was loaded with 250 mL of solution. The pH was adjusted to the desired value by dropwise addition of sulfuric acid or sodium hydroxide. When needed; hydrogen peroxide (24–60 mg/L range) was added. Samples were periodically collected from the reactor and filtered through 0.45 μm nylon filters (Millipore Millex-HN) before analyses. Eventually, in order to prevent the decomposition of organic components after sampling, samples were immediately diluted (1:3 v/v) with methanol.

2.3. Chemical analysis

Pollutants concentration was determined by high performance liquid chromatography. The apparatus was a LaChrom from Merck-Hitachi equipped with autosampler and diode array detector. A reverse phase column LiChrospher® 100 RP-18 (5 μm) was used and a mixture of 1 mM sulfuric acid and acetonitrile (50% v/v) were employed as a mobile phase in a flow rate of 1.2 mL/min.

The variation of the dissolved organic carbon (DOC) was measured using a Shimadzu-V_{CHP} TOC analyzer which was fed by an autosampler system. The concentration of iron species in the water was measured according to the o-phenanthroline standardized spectrometric procedure (ISO 6332) [27]. Hydrogen peroxide consumption was checked by the use of colorimetric strips (MQuant Peroxide Test).

3. Results and discussion

3.1. ZVI process with distilled water

A first experiment was carried out with Milli Q water at the natural pH solution (3.5) in the absence of hydrogen peroxide. These conditions are expected to be favorable for the reducing phase, as the photo-Fenton process cannot happen without peroxide. Fig. 3 shows that the process was clearly inefficient, as pollutants removal was negligible after 90 min and only a slight decrease (ca. 5%) of nitrobenzoic acid was observed. In agreement, the amount of iron released into the solution was very low (less than 0.3 mg/L).

When low amounts of hydrogen peroxide were added (two additions of 12 mg/L each, at 5 and 30 min of reaction, the behavior was clearly different (Fig. 4). In this case, a significant concentration of iron was found in the solution (up to 3.5 mg/L, which is an order of magnitude above the previous experiment), most probably due to oxidation of ZVI by the peroxide. All five pollutants were removed in different degrees: ca. 75% of elimination were reached for benzoic acid, acetaminophen and caffeine; p-toluensulfonic acid also yielded the same photodegradation although reaction was slower in the initial stages. On the contrary, nitrobenzoic acid was the most recalcitrant to this process. In this second experiment, the predominance of a photo-Fenton based oxidative phase can be postulated since the order of reactivity is ruled by the presence of deactivating groups in the aromatic ring (sulfonic or nitro) [28].

It is worthy to indicate that the presence of activated carbon has been used in combination with ZVI to enhance its corrosion, and hence, reductive processes. In fact, some papers describe this phenomenon [29]. However, for this purpose, the C:ZVI ratio is very high when compared with the commercial steel wool employed in this work (0.1–0.15% of carbon). For this reason, although micro-electrolysis processes cannot be completely ruled out, it is very unlikely to be relevant in this case.

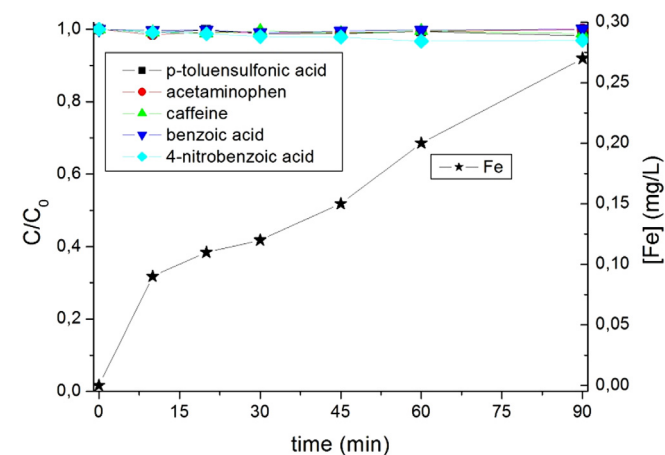


Fig. 3. Plot of the relative concentration of the studied pollutants vs. time in the presence of ZVI in Milli-Q water at pH = 3.5. Concentration of iron in solution is shown in the right axis.

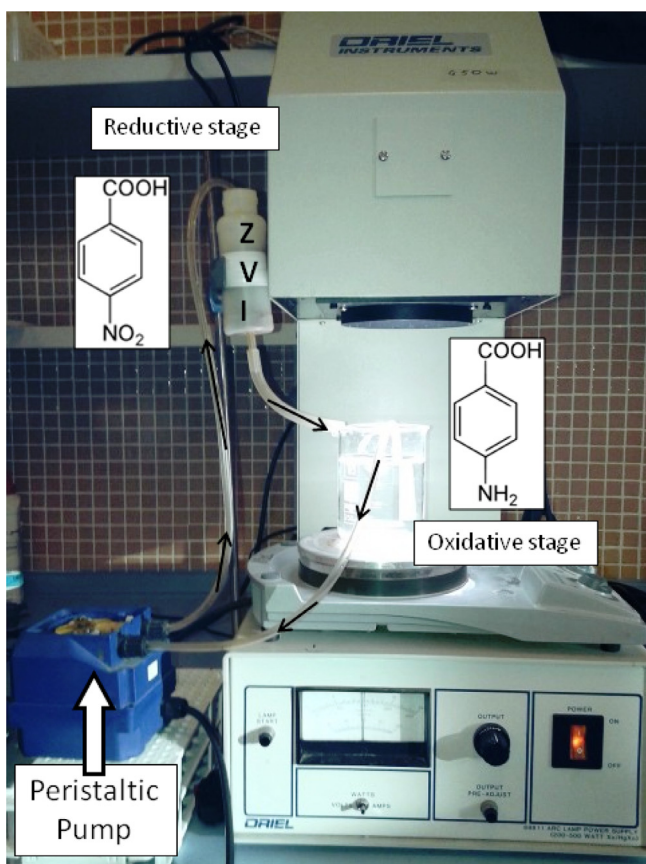


Fig. 2. Experimental set-up employed in the process.

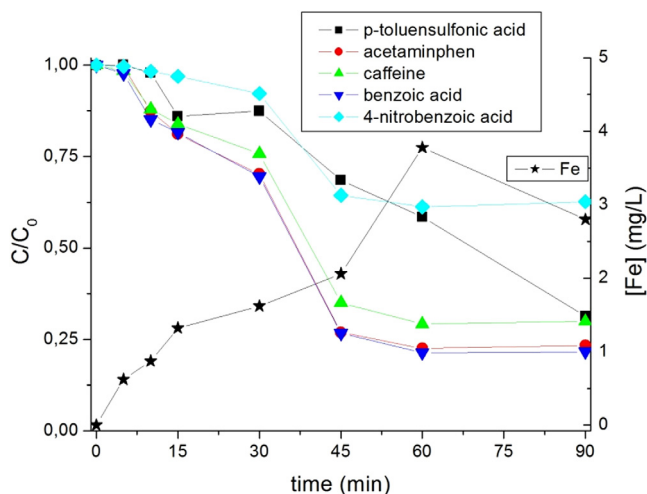


Fig. 4. Plot of the relative concentration of the studied pollutants vs. time in the presence of ZVI in Milli-Q water at pH = 3.5, upon addition of hydrogen peroxide (two additions of 12 mg/L each). Concentration of iron in solution is shown in the right axis.

3.2. ZVI process with tap water

Experiments were repeated using tap water, as the presence of salts might play a paramount role on the corrosion of iron. The initial pH values used were 3.5 (initial pH of the target mixture), 7.5 (natural pH of tap water) and 5.5 (an intermediate value). Fig. 5 shows results obtained at each pH value, both in the absence and in the presence of H₂O₂. At pH = 3.5 and without H₂O₂, corrosion of iron was increased (more than 12 mg/L), in sharp contrast with experiments carried out in distilled water. This difference may be attributed to the presence of dissolved salts in the tap water, as ions behave as electrolytes in the solution, thus favoring iron corrosion, as reported by Triszcz et al. [21].

Significant removal of p-nitrobenzoic was observed; interestingly, this compound was the more reluctant to oxidation. Hence, reduction of p-nitrobenzoic could explain this behavior (see Section 3.3), in agreement with the predominance of a reductive mechanism in the absence of peroxide. These results clearly indicate that salts are necessary for the electrochemical process that results in ZVI oxidation and concomitant reduction of p-nitrobenzoic acid.

Although the same qualitative behavior could be observed at pH = 5.5 and 7.5 (important iron release, removal of p-nitrobenzoic acid and no effect on the other pollutants), the rate of removal of p-nitrobenzoic acid increased with increasing pH (approximately 40%, 60% and 80% after 90 min of treatment at pH = 3.5, 5.5 and 7.5 respectively). This could be explained by a competitive effect of H₂ evolution (Eq. (1)) with the reduction of p-nitrobenzoic acid. At acidic medium, the presence of higher concentrations of H⁺ makes Eq. (1) more likely, while the reverse is true at neutral medium [21].

A new set of experiments, was conducted under the same conditions but in the presence of H₂O₂ (12 mg/L at $t = 5$ min and $t = 30$ min). Fig. 5 (right column) shows very similar behavior as Fig. 4 (in Milli Q water). This means that the photo-Fenton process is clearly predominating vs. the reductive step. There was a decrease in the degradation rate of the pollutants at increasing pH values, which is in agreement with the behavior on the Fenton system (pollutants removal after 45 min was between 30 and 70% at pH = 3.5, ca. 10% for pH = 5 and negligible at pH = 7.5). However, in experiments carried out at pH 5.5 and 7.5 there was an enhanced degradation of p-nitrobenzoic acid after $t = 45$ min, in

coincidence with the exhaustion of H₂O₂ from the reaction medium. This shows that beyond this point, the reductive process became predominant. This result is interesting as it shows that oxidation/reduction can be combined by tuning the experimental conditions. Putting all the results together, acidic pH and the presence of hydrogen peroxide favor the oxidative photo-Fenton process, whereas mild pH, high conductivity and the absence of H₂O₂ shift the process towards the reductive stage.

3.3. Mechanistic issues

At this point, it is interesting to study the intermediates formed in the removal of p-nitrobenzoic acid under reductive conditions. HPLC analysis of treated samples allowed identification of 4-aminobenzoic acid by comparison of its retention time with that of a standard solution of this compound. This by-product is in agreement with literature, as p-aminophenol was detected in the reduction of p-nitrophenol [30] and aniline was the major reduction by product of nitrobenzene [31]. In fact, we have proven with our system that under the reductive conditions nitrobenzene undergoes aniline as the only product. All these data prove that ZVI is able to reduce the nitro group under selected experimental conditions (Fig. 6).

The ZVI-mediated stage had two desirable effects on the overall process: (a) continuous release of iron in the solution, and (b) conversion of deactivating nitro groups into activating amino groups, thus turning the aromatic rings more prone to chemical oxidation triggered by HO· radicals. Iron corrosion might help to keep a steady concentration of iron in solution (4–12 mg/L according to Fig. 5), by generating *in situ* new iron cations that replace the ones precipitating as hydroxides or oxyhydroxides (which are photochemically much less active). Hence, once the parent pollutant has been reduced, hydrogen peroxide can be added to drive a mild photo-Fenton process.

In order to check that 4-aminobenzoic can be more easily oxidized than 4-nitrobenzoic acid, a solution containing same amount of both compounds (25 mg/L) was submitted to a photo-Fenton process at an initial pH of 5.5, an iron concentration of 5 mg/L (added as ferrous sulfate) and an amount of hydrogen peroxide of 60 mg/L. The relative concentration of both chemicals vs. time can be shown in Fig. 7. Data was fitted to pseudo-first order kinetics, and the k values were obtained from the slope of the plot. In fact, degradation of aminobenzoic acid was faster than that of nitrobenzoic acid; the rate constant obtained for the first compound (0.026 min⁻¹) being three times higher than the one obtained for the nitro compound (0.0087 min⁻¹). This 1:3 ratio is in agreement with data reported by Buxton et al. [32] where the bimolecular kinetic constant obtained for the reaction of ·OH with the amino compound ($8.2 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$) was 3.2 higher than that measured for the nitrobenzoic acid ($2.6 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$).

3.4. Coupled processes

A logical step forward consists in coupling both processes: first a ZVI-mediated reduction stage to deal with the nitro group in the absence of H₂O₂, followed by a photo-Fenton based oxidation upon addition of peroxide after exhaustion of the parent nitro compound. With this configuration, the photo-Fenton stage profits from the iron released in the first stage. As only p-nitrobenzoic acid suffered reduction, in order to test the combined setup for this particular pollutant, the mixture of 5 pollutants was substituted by another one containing only 4-nitrobenzoic acid at a concentration equivalent to the cumulative amount of chemicals in the mixture (25 mg/L). Another important issue to be addressed was the operating pH, as high values are beneficial for the ZVI-reductive stage and the reverse is true for photo-Fenton process; furthermore,

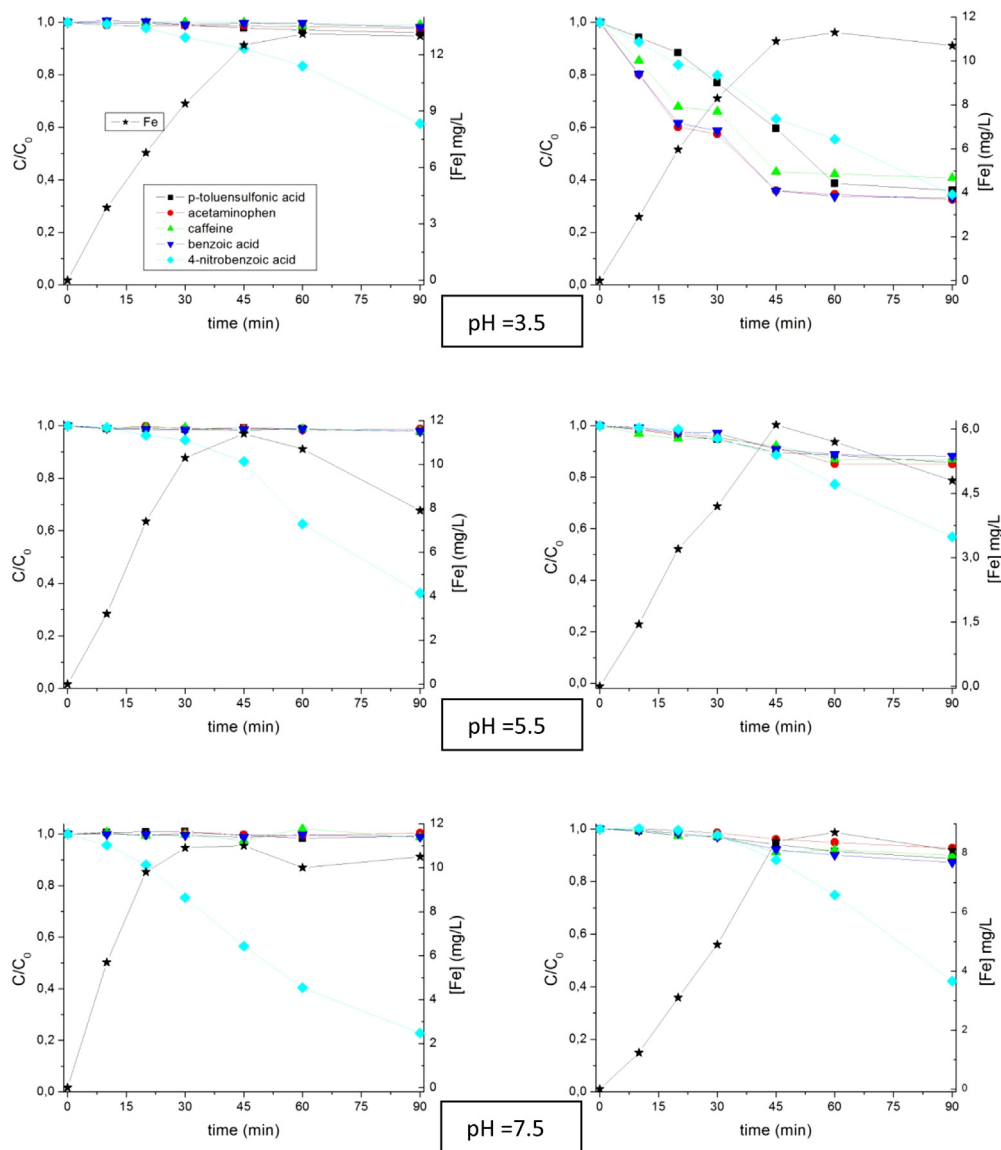


Fig. 5. Plot of the relative concentration of the studied pollutants vs. time in the presence of ZVI in tap water at three different pH: 3.5 (above), 5.5 (middle) and 7.5 (bottom). Experiments in the left column are carried out in the absence of hydrogen peroxide, while those on the right were performed with this reagent (24 mg/L, two additions of 12 mg/L each). Concentration of iron in solution is shown in the right axis.

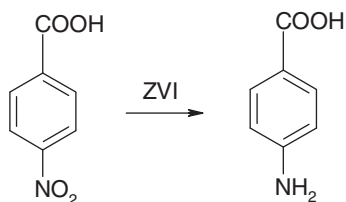


Fig. 6. Reduction of p-nitrobenzoic acid to form p-aminobenzoic acid.

pH is increased in the ZVI process. For this reason, an initial pH of 5.5 was selected.

Regarding to DOC, the initial value was 15.6 mg/L and it remained constant throughout the reductive step (nitrobenzoic to aminobenzoic acid); this is an expectable behavior as the amount of carbon did not vary as any CO_2 evolution occurred under those conditions. Furthermore, this allowed ruling out the possible adsorption of pollutants onto the solid. In the

photo-Fenton phase some DOC decrease was observed (10%); this indicates that although pollutant removal was efficient, mineralization is a more difficult goal to be achieved.

As shown in Fig. 8, complete reduction of p-nitrobenzoic acid was achieved after 120 h re-circulation through the steel wool. At same time, the oxidation of ZVI released iron in solution in an appreciable amount; the final pH was 6.7. At this point, hydrogen peroxide (30 mg/L) was added, recirculation stopped and the cylindrical reactor was irradiated to run a photo-Fenton reaction. Even under these unfavorable conditions (near neutral pH, high initial pollutant concentration, final $[\text{Fe}] = 4 \text{ mg/L}$), aminobenzoic acid was removed (80%) after 60 min of photo-Fenton process, thus showing that this procedure might be applicable and deserves further research.

For the sake of comparison, the same procedure was performed but in the absence of illumination (Fenton process). As expected, results were the same in the reductive stage since, in both cases, it was conducted without irradiation. In sharp contrast, the oxidative reaction was much slower in the dark; this is a logical result as

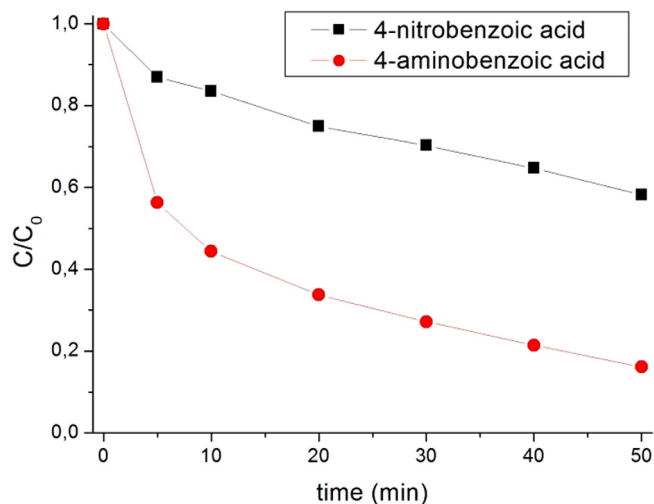


Fig. 7. Plot of the relative concentration of 4-nitrobenzoic acid and 4-aminobenzoic acid along a photo-Fenton process. The initial concentration of hydrogen peroxide was 60 mg/L.

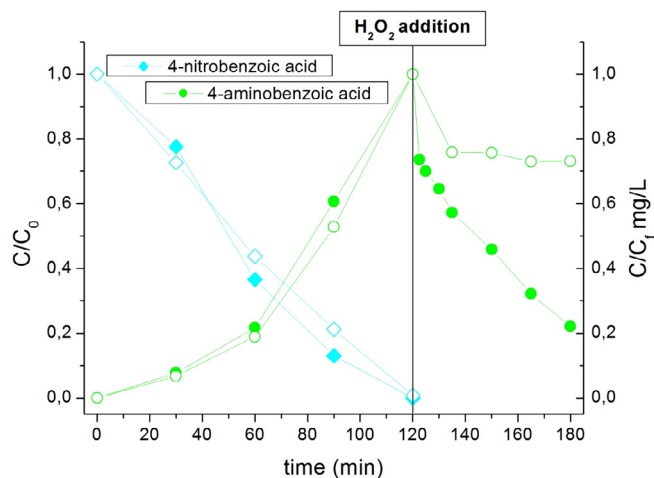


Fig. 8. Plot of the relative concentration of 4-nitrobenzoic acid and 4-aminobenzoic acid along combined processes consisting of a reductive stage (ZVI) followed by an oxidative stage upon H_2O_2 addition (30 mg/L). Dark Fenton results are shown with empty symbols, whereas photo-Fenton results are presented with full symbols.

photo-Fenton is well established to be more efficient than dark Fenton process. Moreover, DOC analyses showed no decrease during dark Fenton process, while a DOC decrease of ca. 10% was observed after 60 min of irradiation.

3.5. Perspectives and future challenges

Some of the potential inconveniences could be overcome if the pollutants are found at low concentrations (emerging pollutants are typically in the $\mu\text{g/L}$ or even ng/L range [33]); in this case, low amounts of iron and hydrogen peroxide would be needed and the reaction time could be lower.

Another concern is the release of iron below the discharge limits. Regarding this issue, iron hydroxides and oxyhydroxides were easily settled down: when the pump was stopped, dissolved iron concentration decreased in the reservoir to reach values below 1 mg/L. Removal of this small amount of iron based sludge should be taken into account when designing a pilot reactor to be applied in real situation.

The low hydrogen peroxide concentration used in this work satisfies the requirement of 'mild conditions' and could be even decreased with pollutants at $\mu\text{g/L}$ concentrations. To study the effect of hydrogen peroxide is a complex issue as, although reaction kinetics could be enhanced with higher peroxide concentrations, it has also been reported that an excess of hydrogen peroxide concentration results in a loss of efficiency due to the scavenging of HO^\cdot radicals by H_2O_2 . Moreover, large amounts of oxygen can be generated and the reaction rates remain almost constant above certain value of peroxide concentration [34]. Furthermore, in view of combining reducing and oxidizing steps, H_2O_2 should be dosed to be completely consumed in the oxidative process, allowing a peroxide free effluent to reach the ZVI cartridge.

Finally, the process could also benefit from slight pH modifications or addition of iron-complexing substances that can extend the efficient pH domain for photo-Fenton to circumneutral values [35]. These alternatives deserve to be explored in the future.

4. Conclusions

A procedure combining reductive and oxidative stages has been demonstrated to be promising to deal with pollutants difficult to oxidize. It has the advantage of performing the reducing and oxidizing stages in different parts of the reactor, making possible to favor each stage (or even the overall performance of combined process) by tuning the experimental conditions. In line with the aim of this MS, this is a very niche application of AOPs and maybe meaningful for a limited number of compounds, namely those reluctant to oxidation, such as p-nitrobenzoic acid. Moreover, we have now demonstrated that the reductive stage is not a drawback for the photo-Fenton treatment of other compounds. In fact, ZVI-photo-Fenton coupling could be even useful in other situations: for instance, when applying photo-Fenton as tertiary treatment to remove trace amounts of xenobiotics. In this case, strong acidification should be avoided and the choice is circumneutral pH conditions. ZVI constitutes a continuous source of iron to replace the loss by precipitation. Furthermore, the use of iron wool in a cartridge might be advantageous in comparison with particulate iron in slurry for photochemical processes as light scattering by suspended particles could be overcome.

Certainly, to assess the real applicability of the process further research is still required; the investigation should involve: (a) different designs of reactor setup, (b) the optimization of operational parameters such as pH and/or H_2O_2 dosage, (c) the analysis of the performance at low concentrations of pollutants, (d) the use of novel trends to extend photo-Fenton at mildly acidic pH (e.g. complexing agents) and (e) the application of this methodology to other families of compounds that cannot be easily oxidized (e.g. perfluorinated molecules such as flame retardants or chlorinated organic compounds).

Acknowledgments

Authors want to acknowledge the financial support of Spanish Ministerio de Economía y Competitividad (CTQ2015-69832-C4-4-R), European Union (645551-RISE-2014, MAT4TREAT), Argentinean CONICET Project (PIP: #112-2013-01-00236CO) and Argentinean UNLP (Project No. I174). F.S. García Einschlag is a research member of CONICET.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.04.114>.

References

- [1] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84.
- [2] J.J. Pignatello, Dark and photoassisted Fe³⁺-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, *Environ. Sci. Technol.* 26 (1992) 944–951.
- [3] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, *Catal. Today* 147 (2009) 1–59.
- [4] A. Zapata, I. Oller, E. Bizani, J.A. Sánchez-Pérez, M.I. Maldonado, S. Malato, Evaluation of operational parameters involved in solar photo-Fenton degradation of a commercial pesticide mixture, *Catal. Today* 144 (2009) 94–99.
- [5] J. Soler, A. García-Ripoll, N. Hayek, P. Miró, R. Vicente, A. Arques, A.M. Amat, Effect of inorganic ions on the solar detoxification of water polluted with pesticides, *Water Res.* 43 (2009) 4441–4450.
- [6] I. Carra, L. Santos-Juanes, F.G. Ación Fernández, S. Malato, J.A. Sánchez-Pérez, New approach to solar photo-Fenton operation. Raceways ponds as tertiary treatment technology, in: *J. Hazard. Mater.* 279 (2014) 322–329.
- [7] L. Santos-Juanes, M.M. Jordá, Ballesteros Martín, E. Ortega Gómez, A. Cabrera Reina, I.M. Román Sánchez, J.L. Casas López, J.A. Sánchez Pérez, Economic evaluation of the photo-Fenton process. Mineralization level and reaction time: the keys for increasing plant efficiency, *J. Hazard. Mater.* 186 (2011) 1924–1929.
- [8] E. Ortega-Gómez, E. Moreno Úbeda, J.D. Álvarez Hervás, J.L. Casas López, L. Santos-Juanes, J.A. Sánchez Pérez, Automatic dosage of hydrogen peroxide in solar photo-Fenton plants: development of a control strategy for efficiency enhancement, *J. Hazard. Mater.* 237–238 (2012) 223–230.
- [9] M. Terasaki, M. Makino, N. OrihisaTatarazako, Acute toxicity of parabens and their chlorinated by-products with *Daphnia magna* and *Vibrio fischeri* bioassays, *J. Appl. Toxicol.* 29 (2009) 242–247.
- [10] D. Juretic, H. Kusic, N. Koprivanac, A. LoncaricBozic, Photooxidation of benzene structured compounds: influence of substituent type on degradation kinetic and sum water parameters, *Water Res.* 46 (2012) 3074–3084.
- [11] N. Klamerth, S. Malato, A. Agüera, A. Fernández-Alba, Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison, *Water Res.* 47 (2013) 833–840.
- [12] J. Gomis, L. Carlos, A. Bianco Prevot, A.C.S.C. Teixeira, M. Mora, A.M. Amat, R. Vicente, A. Arques, Bio-based substances from urban waste as auxiliaries for solar photo-Fenton treatment under mild conditions: optimization of operational variables, *Catal. Today* 240 (2015) 39–45.
- [13] I. Carra, S. Malato, M. Jiménez, M.I. Maldonado, J.A. Sánchez Pérez, Microcontaminant removal by solar photo-Fenton at natural pH run with sequential and continuous iron additions, *Chem. Eng. J.* 235 (2014) 132–140.
- [14] X. Guan, Y. Sun, H. Qin, J. Li, I.M.C. Lo, D. He, H. Dong, Review. The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: the development in zero-valent iron technology in the last two decades (1994–2014), *Water Res.* 75 (2015) 224–248.
- [15] G.B. Ortiz de la Plata, O.M. Alfano, A.E. Cassano, 2-Chlorophenol degradation via photo-Fenton reaction employing zero valent iron nanoparticles, *J. Photochem. Photobiol. A: Chem.* 233 (2012) 53–59.
- [16] F. Fu, D.D. Dionysiou, H. Liu, The use of zero-valent iron for groundwater remediation and wastewater treatment: a review, *J. Hazard. Mater.* 267 (2014) 194–205.
- [17] C. Noubactep, Metallic iron for water treatment: a critical review, *Clean Soil Air Water* 41 (2013) 702–710.
- [18] Y. Segura, F. Martínez, J.A. Melero, J.L.G. Fierro, Zero valent iron (ZVI) mediated Fenton degradation of industrial wastewater: treatment performance and characterization of final composites, *Chem. Eng. J.* 269 (2015) 298–305.
- [19] R. Li, X. Xin, M. Megharaj, R. Naidu, Z. Chen, Heterogeneous Fenton oxidation of 2,4-dichlorophenol using iron-based nanoparticles and persulfate system, *Chem. Eng. J.* 264 (2015) 587–594.
- [20] J.M. Calo, L. Madhavan, J. Kirchner, E.J. Bain, Arsenic removal via ZVI in a hybrid spouted vessel/ fixed bed filter system, *Chem. Eng. J.* 189–190 (2012) 237–243.
- [21] J.M. Triszcz, A. Porta, F.S. García Einschlag, Effect of operating conditions on iron corrosion rates in zero-valent iron systems for arsenic removal, *Chem. Eng. J.* 150 (2009) 431–439.
- [22] B. Morgan, O. Lahav, The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O₂ in aqueous solution – basic principles and a simple heuristic description, *Chemosphere* 68 (2007) 2080–2084.
- [23] H.F. Schroder, R.W. Meesters, Stability of fluorinated surfactants in advanced oxidation processes – a follow up of degradation products using flow injection mass spectrometry, liquid chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry, *J. Chromatogr. A* 1082 (2005) 110–119.
- [24] A.M. Amat, A. Arques, M.A. Miranda, F. Lopez, Use of ozone and/or UV in the treatment of effluents from board paper industry, *Chemosphere* 60 (2005) 1111–1117.
- [25] W. Wang, K. Kannan, Fate of parabens and their metabolites in two wastewater treatment plants in New York State, United States, *Environ. Sci. Technol.* (2016), <http://dx.doi.org/10.1021/acs.est.5b05516>.
- [26] A. Boxall, Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters, 2008, pp. 1–28.
- [27] Standard Methods Online – Standard Methods for the Examination of Water and Wastewater (2016). <<http://standardmethods.org/>>.
- [28] V. Kavitha, K. Palanivelu, Degradation of nitrophenols by Fenton and photo-Fenton processes, *J. Photochem. Photobiol. A: Chem.* 170 (2005) 83–95.
- [29] P. Liu, J. Keller, W. Gernjak, Enhancing zero valent iron based natural organic matter removal by mixing with dispersed carbon cathodes, *Sci. Total Environ.* 550 (2016) 95–102.
- [30] K. Urkude, S.R. Thakare, S. Gawande, An energy efficient photocatalytic reduction of 4-nitrophenol, *J. Environ. Chem. Eng.* 2 (2014) 759–764.
- [31] Y. Mu, H.Q. Yu, J.C. Zheng, S.J. Zhang, G.P. Sheng, Reductive degradation of nitrobenzene in aqueous solution by zero-valent iron, *Chemosphere* 54 (2004) 789–794.
- [32] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [33] K.E. Murray, S.B. Thomas, A.A. Badour, Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment, *Environ. Pollut.* 158 (2010) 3462–3471.
- [34] L. Santos-Juanes, J.L.G. Sánchez, J.L.C. López, I. Oller, S. Malato, J.A. Sánchez Pérez, Dissolved oxygen concentration: a key parameter in monitoring the photo-Fenton process, in: *Appl. Catal. B: Environ.* 104 (2011) 316–323.
- [35] J. Gomis, L. Carlos, A. Bianco Prevot, A.C.S.C. Teixeira, M. Mora, A.M. Amat, R. Vicente, A. Arques, Bio-based substances from urban waste as auxiliaries for solar photo-Fenton treatment under mild conditions: optimization of operational variables, *Catal. Today* 240 (2015) 39–45.