The final publication is available at

https://doi.org/10.1016/j.cej.2016.04.114

Additional Information

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

L. Santos-Juanes, A.M. Amat, A. Arques

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

To whom correspondence should be adressed: Phone: +34 966528417. Fax: +34 966528438. E-mail: aarques@txp.upv.es.

Abstract

An iron-based photochemical process able to act via reductive and oxidative phases 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 in an illuminated reservoir. 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-toluensulfonic 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 H_2O_2 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 phases is meaningful: a ZVI-based reduction followed by a photo-Fenton like-oxidation was employed to remove this pollutant from tested solutions.

Graphical abstract
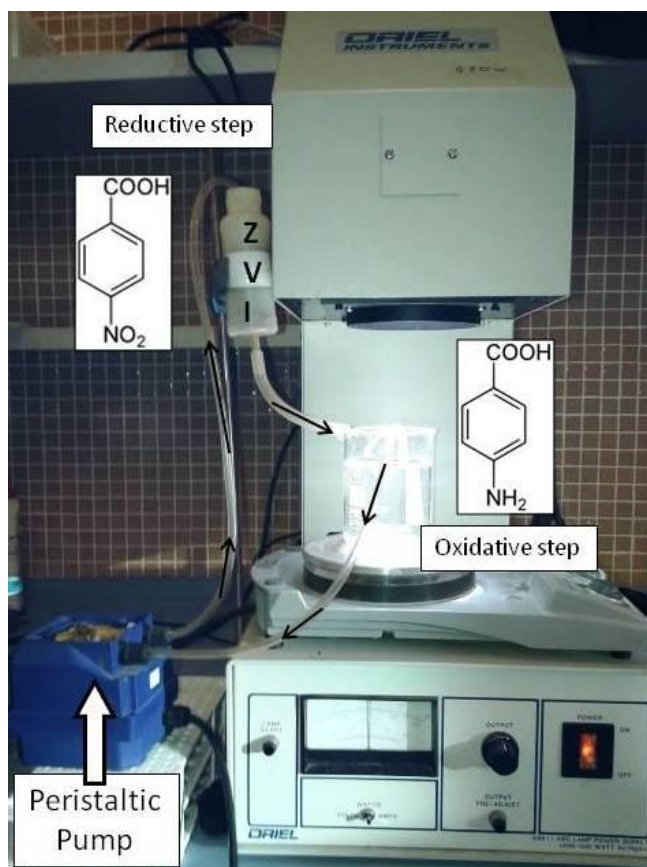
Highlights

An integrated process combining oxidizing and reducing steps has been developed

Variation of experimental conditions allows choosing oxidizing or reducing steps

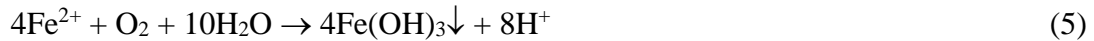This methodology might be useful to deal pollutants reluctant to oxidation

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 [2] and hence, increasing attention has been paid by researchers to photo-Fenton during the last 20 years. Process variables such as pH, effect of anions or cations, temperature, light sources, different reactors, process costs or automatization have been widely investigated [3-7].

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 [8]) or its low reactivity due to the presence of electron-withdrawing groups that deactivate electrophilic attack of the reactive species (e.g. nitro groups, sulfonates, cyano group) [9]. 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 [10, 11]), makes these approaches unattractive and requires exploration of alternative processes.

Zero valent iron (ZVI) is a process based on the ability of elemental iron to act as reducing agent (standard redox potential of -0.44 V), which can be employed for decontamination

3

of water and groudwater [12,13]. It has been used to remove different types of pollutants from water such as chlorinated compounds, arsenic, nitrate, dyes or nitro-aromatic compounds [14-16]. The reaction mechanism of contaminants reduction by ZVI is complex [17] and, at least, the manifold of equations given below (1-8) should be considered [18]. As can be inferred, pH of the medium plays an important role, especially regarding to the formation of precipitates (reactions 3-5). Furthermore, it has been reported that pH has a significant effect on the oxidation of more soluble Fe(II) species into Fe(III) [19].

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow \tag{1}$$

$$2Fe^0 + O_2 + H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{2}$$

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2\downarrow + 2H^+ \tag{3}$$

$$6Fe^{2+} + O_2 + 6H_2O \rightarrow 2Fe_3O_4\downarrow + 12H^+ \tag{4}$$

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3\downarrow + 8H^+ \tag{5}$$

$$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4FeOOH\downarrow + 8H^+ \tag{6}$$

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{7}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \tag{8}$$

As iron is oxidized, ferrous salts are released into the solution. In this way, oxidizing phases, based on (photo)-Fenton chemistry may also occur, in particular if hydrogen peroxide is added to the reaction mixture [20]. In fact, both processes could coexist, but one of them would be favored, according to the experimental conditions. 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 [9]: a first reducing step will be applied to modify reluctant substances 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 will be employed in the photo-Fenton process. However. Most of the studies using ZVI as source of iron for photo-Fenton involves the coexistence of iron and the pollutant in the same reactor, involving that the reducing phase is suppressed, hydrogen peroxide is employed in corrosion of iron and the presence of solids results in light scattering. For this purpose, it is necessary to develop a methodology that separates reducing and oxidizing steps.

With this background, the aim of this work is to study a combined ZVI-photo-Fenton process. As factors influencing the photo-Fenton process are well-known, special emphasys will be made on the reductive phase. For this purpose a mixture of five pollutants, p-toluensulfonic acid, benzoic acid, p-nitrobenzoic acid, acetaminophen and caffeic (see Figure 1 for structures) has been employed. They are aromatic compounds bearing different functional groups. These compounds present, at least, an acid group and a nitro and a sulfonate group. 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.

2. Experimental

2.1. Reagents.

High purity acetaminophen, caffeine, benzoic acid, p-nitrobenzoic acid and p-toluensulfonic acid and were supplied by Sigma-Aldrich. Sulphuric acid (96%), ferrous sulphate (99%), hydrogen peroxide (30%) and acetonitrile (HPLC grade) were purchased by Panreac. The water matrix used was Milli-Q grade and tap water (pH = 7.4, inorganic carbon = 52 mg/L, conductivity = 510 μS/cm). 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 (Figure S1)

2.2. Chemical reactions

The experimental set-up employed in the combined ZVI-photo-Fenton process can be observed in Figure 2. The steel wool was placed 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 wood at a flow rate of 20 mL/min using a peristaltic pump PR7 (SEKO). A solar simulator (Oriel Instruments, Model 81160 equipped with a 300W xenon lamp) whose emission spectrum closely matches the solar one was employed to irradiate the open glass reactor.

The target solution consisted in a mixture of the five pollutants at an initial concentration of 5 mg/L each. For each experiment, the reactor was loaded with 250 mL of solution. The pH was adjusted to the desired value by dropwise addition of sulphuric acid or sodium hydroxide. When needed, hydrogen peroxide (12-60 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, the sample was diluted (1:3 v/v) with methanol in quench the photo-Fenton process.

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 (5μm) was used and a mixture of 1mM 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).

3. Results and discussion

3.1. Simultaneous processes. Affecting factors.

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. Figure 3 shows that the process was clearly inefficient, as pollutants removal was negligible after 90 min, as only a slight decrease (ca. 5%) of nitrobenzoic acid was observed. In agreement, the amount of iron released into the solution was wery low (less than 0.3 mg/L)

When a low amount of hydrogen peroxide (two additions of 12 mg/L each, one after 5 min of reaction and the second one after 30 min) was added, the behavior was clearly different (Figure 4). In this case, a significant concentration of iron was found in the

solution (until 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, acetaminophen and caffeine; p-toluensulfonic also yield the same photodegradation although reaction was slower in the initial stages. On the contrary, nitrobenzoic was the most recalcitrant to this process. In this second experiment, the predominance of a photo-Fenton based oxidative phase can be postulated and the order of reactivity is ruled by the presence of deactivating groups in the aromatic ring (sulfonic or nitro) [21, 22]

Experiments were repeated using tap water, as the presence of salts might play a paramount role on the corrosion of iron. The pH was adjusted to 3.5 (which was the pH of distilled water), 7.5 (natural pH of tap water) and to an intermediate value, 5.5. Figure 5 shows results obtained at all those pH and with or without H_2O_2. At pH = 3.5 and without H_2O_2, corrosion of iron was increased (more than 12 mg/L) because of the presence of electrolytes in the solution that favors iron corrosion, as reported by Triszcz et al. [17]. Significant removal of p-nitrobenzoic was observed; interestingly, this compound was the more reluctant to oxidation. This could be in agreement with the predominance of the reducing step in the absence of peroxide. Hence, reduction of p-nitrobenzoic could explain this behavior, as will be discussed in section 3.2.

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), some quantitative differences could be found: a) the rate of removal of p-nitrobenzoic acid increased with increasing pH and b) the amount of iron in solution slightly decreased with increasing pH. This could be explained by a competitive effect of H_2 evolution (equation

1) with the reduction of p-nitrobenzoic. At acidic medium, the presence of higher concentrations of H^+ makes equation 1 more likely, while the reverse is true at neutral medium [17]. Differences in iron concentration might be attributed either to a faster corrosion of iron at acidic medium or to a lower solubility of these species at neutral pH. In fact, significant pH increase can be observed in all cases (ca. 1 unit) which is in agreement H^+ consumption.

Experiments were repeated at the same pH values in the presence of H_2O_2 (12 mg/L at t= 5 min and t= 30 min). Figure 5 (right column) shows very similar behavior as Figure 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. 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 H_2O_2 from the reaction medium. This shows that beyond this point, the reductive process became predominating. 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 favors the oxidative photo-Fenton process and milder pH, high conductivity and the absence of H_2O_2 shifts the process towards the reductive phase.

3.2. Mechanistic issues

At this stage, 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 retention time with that of a

9

standard solution of this compound. This by-product is in agreement with literature, as p-aminophenol was detected in the reduction of p-nitrophenol [23] and aniline was the major reduction by product of nitrobenzene [24]. 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 (Figure 6).

This reductive step had two desirable effects on the process: a) continuous release of iron in the solution b) conversion of deactivating nitro group into amine, which could be more labile to chemical oxidation. Iron corrosion might help to keep a certain concentration of iron in solution (4 to 12 mg/L according to Figure 5), generating *in situ* new iron cations, which replaces the ones precipitating as photo-chemically non-active oxides or hydroxides. 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 that 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 5mg/L (added as ferrous sulphate) and an amount of hydrogen peroxide of 60 mg/L. The relative concentration of both chemicals vs. time can be shown in Figure 7. Data was fitted to a pseudo-first order kinetics, and the k values were obtained from the slope of the plot. In fact, degradation of aminobenzoic was faster than nitrobenzoic acid; the rate constant obtained for the first compound ($0.026 \, min^{-1}$) was trice higher than for the nitro compound ($0.0087 \, min^{-1}$). This 1:3 ratio is in agreement with data reported by Buxton el al [25]

where the bimolecular kinetic constant obtained for the reaction of $\cdot OH$ with the amino compound ($8.2 \cdot 10^9$ Lmol^{-1}s^{-1}) was 3.2 higher than that measured for the nitrobenzoic acid ($2.6 \cdot 10^9$ Lmol^{-1}s^{-1}).

3.3. Coupled processes

A logical step forward consists in coupling both processes: first a ZVI reducing step to deal with the nitro group in the absence of H_2O_2, followed by a photo-Fenton based oxidation upon addition of peroxide after exhaustion of the parent nitro compound, also using the iron released in the first stage. As only p-nitrobenzoic suffered reduction, the mixture of 5 pollutants was substituted by another one containing only 4-nitrobenzoic at a concentration equivalent 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 step and the reverse is true for photo-Fenton; furthermore, pH is increased in the ZVI process. For this reason, an initial pH of 5.5 was selected.

As shown in Figure 8, complete reduction of p-nitrobenzoic acid was achieved after 120 hours re-circulation through the steel wool. At same time, the oxidation of the 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 (neutral pH, high initial pollutant concentration, final [Fe] = 4 mg/L), aminobenzoic acid was removed (80%) after 60 minutes of photo-Fenton process, thus showing that this

procedure might be applicable and deserves further research. For instance, some of the inconveniences could be overcome if the pollutants are found al low concentrations (emerging pollutants are typically in the µg/L or even ng/L range [26]). Addition of controlled amounts of peroxide might allow simultaneous combination of reducing and oxidizing phases at different parts of the reactor; eventually, also pH modification could be necessary. Finally, formation of iron complexes can extend the efficient pH domain for photo-Fenton to circumneutral values, and should be studied in future work [27].

4. Conclusions

A procedure combining reductive and oxidizing steps has been demonstrated to be promising to deal pollutants difficult to oxidize. The procedure has the advantage of performing the reducing and oxidizing steps in different parts of the reactor, and the possibility of favoring each one by tuning the experimental conditions. Furthermore, some drawbacks of using ZVI as source of iron for photo-Fenton can be overcome, such as light scattering by solid iron particles or consumption of H_2O_2 by iron.

However, further research is still required to assess the real applicability of the process: a) optimizing operational parameters such as pH or H_2O_2 dosage, b) studding the performance at low concentrations of pollutants, c) applying novel trends to extend photo-Fenton at mildly acidic pH (e.g. complexing agents) and d) to apply this methodology to other families of compounds that cannot be easily oxidized (e.g perfluorinated molecules such as flame retardants or chlorinated organics).

Acknowledgements:

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

[2] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjiak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, Catal. Today 147 (2009) 1–59.

[3] 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.

[4] 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.

[5] I. Carra, L. Santos-Juanes, F. G. Acién Fernández, S. Malato, J. A. Sánchez-Pérez. New aproach to solar photo-Fenton operation. Raceways ponds as tertiary treatment technology. J. Hazard. Mater. 279 (2014) 322-329.

[6] L. Santos-Juanes Jordá, M.M. 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.

[7] 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.

[8] M. Terasaki, M. Makino, N.orihisa Tatarazako. Acute toxicity of parabens and their chlorinated by-products with Daphnia magna and Vibrio fischeri bioassays. J. Appl. Toxicol. 29 (2009) 242-247.

[9] 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.

[10] 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.

[11] 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.

[12] 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.

[13] C. Noubactep. Metallic iron for water treatment: A critical review. Clean-Soil, air, water 41 (2013) 702-710.

[14] 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.

[15] 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.

[16] 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.

[17] 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

[18] 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.

[19] 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.

[20] 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

[21] V. Kavitha, K. Palanivelu, Degradation of nitrophenols by Fenton and photo-Fenton processes. J. Photochem. Photobiol. A: Chem. 170 (2005) 83–95.

[22] D. Juretic, H. Kusic, N. Koprivanac, A. Loncaric Bozic, Photooxidation of benzenestructured compounds: Influence of substituent type on degradation kinetic and sum water parameters, Water Res. 46 (2012) 3074-3084.

[23] K. Urkude, S.R. Thakare, S. Gawande. An energy efficient photocatalytic reduction of 4-nitrophenol. J. Environ. Chem. Eng.g 2 (2014) 759-764.

[24] 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

[25] 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.

[26] 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.

[27] 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, 39-45, 2015
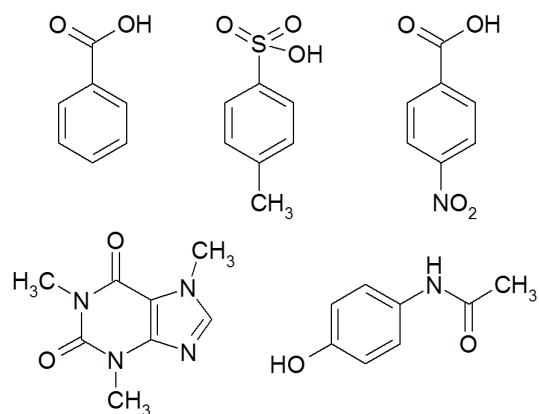
Figure 1: Chemical structures of the pollutants used in this work; from left to right and from top to bottom: Benzoic acid, p-toluensulfonic acid, 4-nitrobenzoic acid, caffeine and acetaminophen.
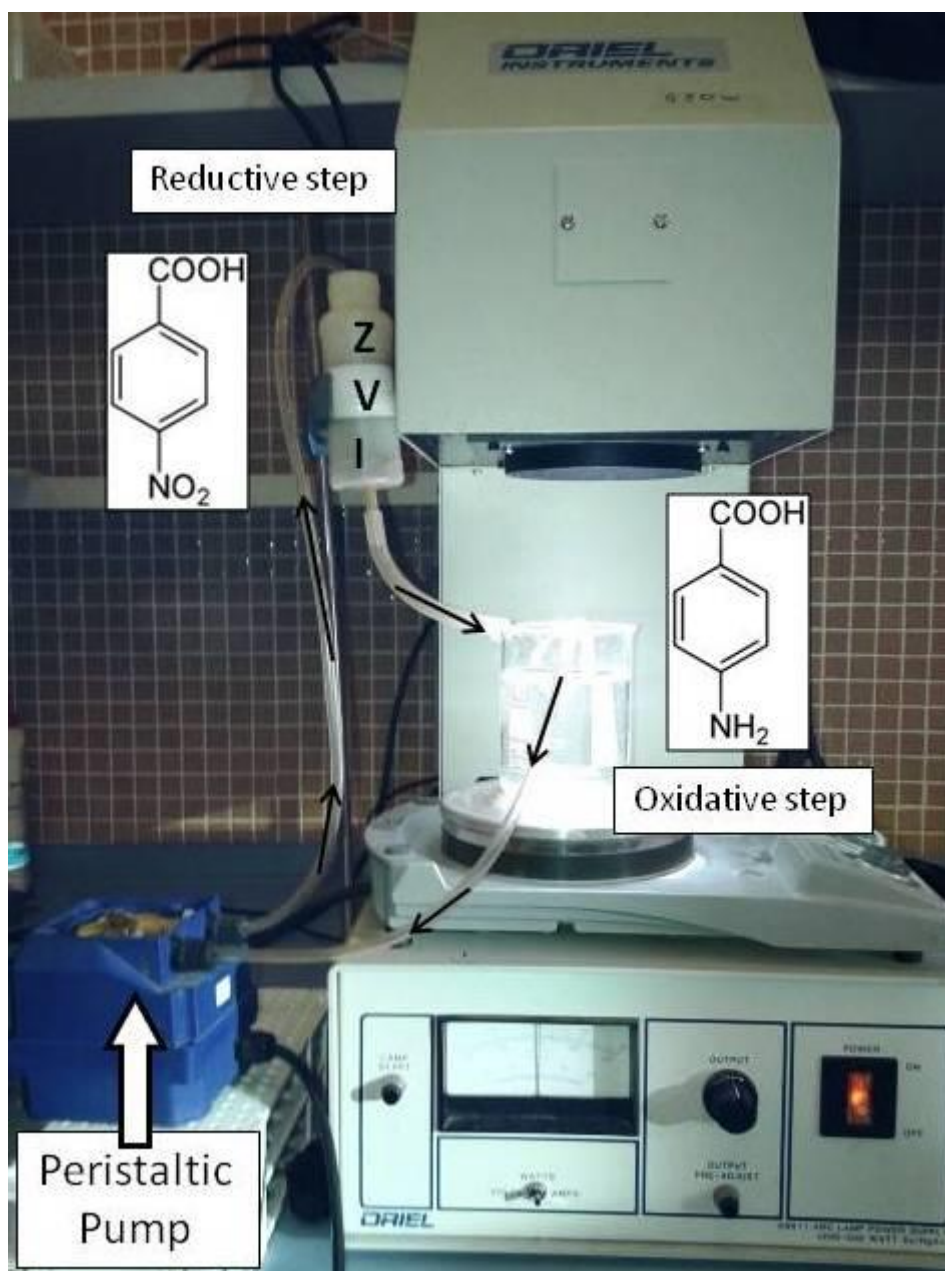
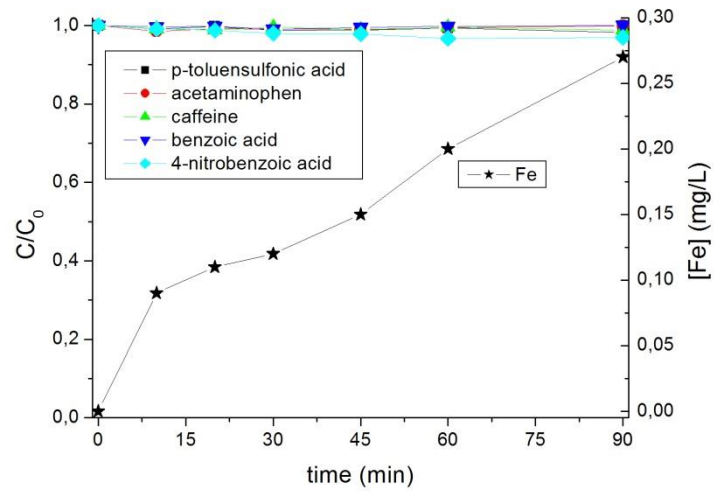Figure 2: Experimental set-up employed in the process

Figure 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.
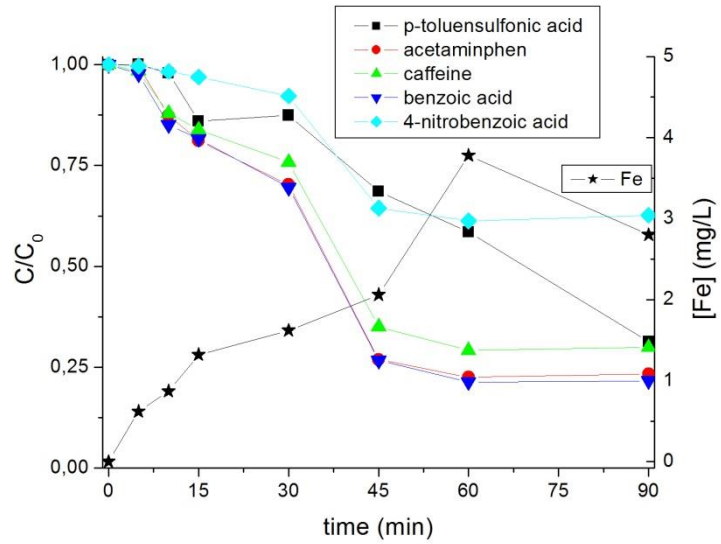
Figure 4: Plot of the relative concentration of the studied pollutants vs. time in the presence of ZVI in Milli-Q water at pH = 3.5, upon addition of hydrogen peroxide. Concentration of iron in solution is shown in the right axis.
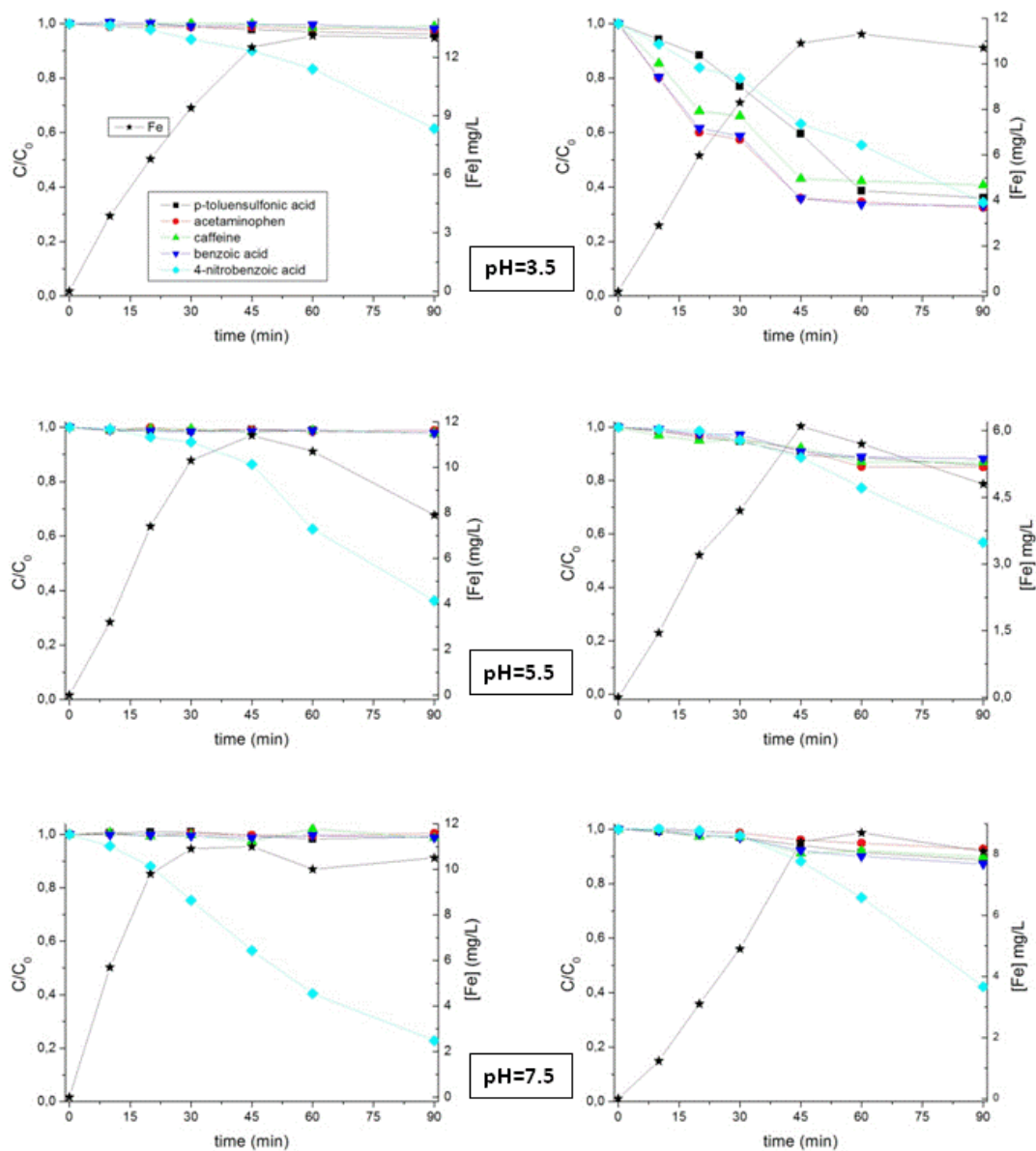
Figure 5: Plot of the relative concentration of the studied pollutants vs. time in the presence of ZVI in tap water at three different pH: 3.5 (above), 5.5 (middle) and 7.5 (bottom). Experiments in the left column are carried out in the absence of hydrogen peroxide, while those on the right were performed with this reagent. Concentration of iron in solution is shown in the right axis.
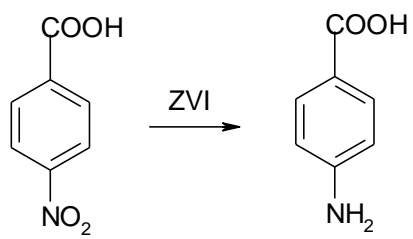
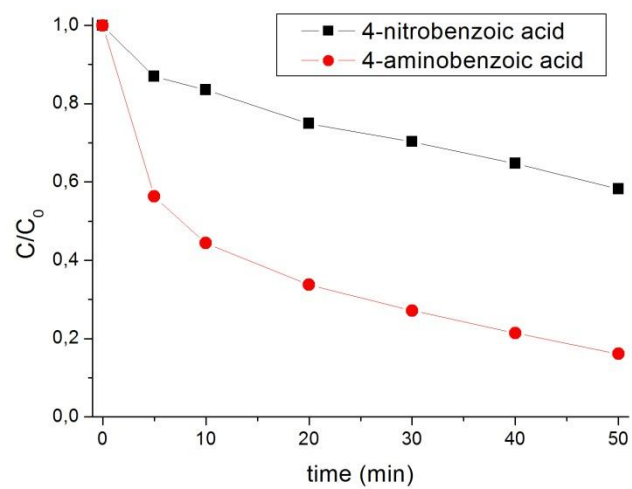Figure 6: Reduction of p-nitrobenzoic acid to form p-aminobenzoic acid.

Figure 7: Plot of the relative concentration of 4-nitrobenzoic acid and 4-aminobenzoic acid along a photo-Fenton process
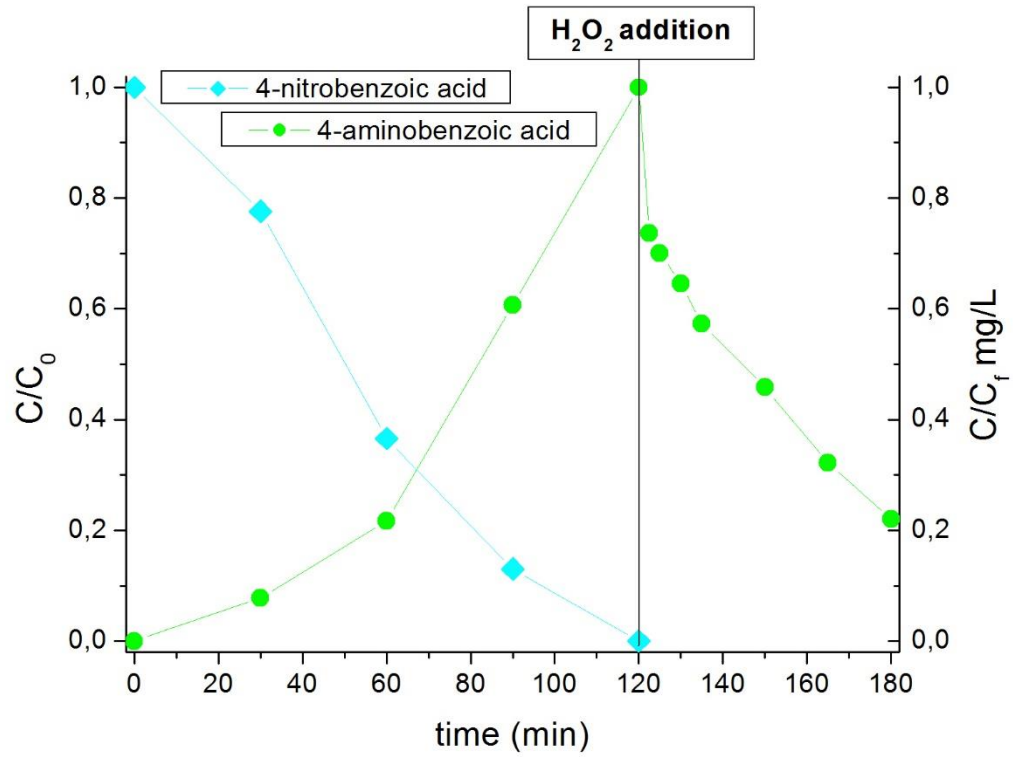
Figure 8: Plot of the relative concentration of 4-nitrobenzoic acid and 4-aminobenzoic acid along a combined process consisting a reductive phase (ZVI) afollowed by an oxidation (photo-Fenton) upon H_2O_2 addition.