Desalination and Water Treatment
www.deswater.com

25 (2011) 210–215
January

1944-3994 / 1944-3986 © 2011 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2011.1445

Application of the photo-Fenton process to the mineralization of phthalic anhydride in aqueous medium

Souhaila Trabelsi-Souissi[a,b,c], Nihal Oturan[a], Nizar Bellakhal[b,c], Mehmet A. Oturan[a]*

[a]*Université Paris-Est, Laboratoire Géomatériaux et Environnement (LGE), 5, bd. Descartes, 77454 Marne-la-Vallée Cedex 2, France*
Tel. +33 (1) 49 32 49 90 65; Fax +33 (1) 49 32 91 37; email: mehmet.oturan@univ-paris-est.fr
[b]*Laboratoire de Chimie Analytique et d'Electrochimie, Faculté des Sciences de Tunis, Campus Universitaire*
2092, El Manar Tunis, Tunisia
[c]*Département de Chimie et Biologie Appliquée, Institut National des Sciences Appliquées et de Technologie, 1080 Tunis, Tunisia*

Recevied 23 December 2009; Accepted in revised form 14 June 2010

ABSTRACT

The oxidation of phthalic anhydride, a chemical widely used as plasticizer, was studied in aqueous medium of pH 3 by the photochemical advanced oxidation process "photo-Fenton" using UV irradiation. This process generates, in a catalytic way, the hydroxyl radicals, a powerful oxidant species, for the oxidation of organic pollutants. The kinetics of the oxidative degradation of phthalic anhydride and that of the solution mineralization was investigated through the effect of some operating parameters such as the ratio $R = [H_2O_2]/[Fe^{3+}]$ and the initial catalyst concentration. The values of $R = 40$ and Fe^{3+} ion (catalyst) concentration of 0.1 mM were found as optimum operating parameters. Mineralization of phthalic anhydride aqueous solution under the optimal conditions was followed by the total organic carbon (TOC) analysis and a high mineralization degree of 98.7% was determined for a treatment time of 2 h.

Keywords: Phthalic anhydride; Hydroxyl radicals; Advanced oxidation process; Photo-Fenton; Mineralization

---

1. Introduction

The increase in industrial and agricultural activities in developing countries requires the use of increasingly high varieties and quantities of synthetic chemicals, such as pesticides, insecticides, dyes and chemical additives. These chemicals are considered toxic when present in the aquatic environment, whether adsorbed on the sediments or retained in living organisms, even at low concentrations because of their negative impact on human health or on the aquatic ecosystem as a whole. Phthalates, which are esters of 1,2-dicarboxylic benzene acids and a linear alcohol more or less branched, belong to this type of pollutants and are considered as emergent contaminants. They are essentially used as plasticizers to increase the flexibility and durability of polyvinyl chloride [1]. Slightly associated to the polymer matrix, phthalates can migrate from various articles made from PVC [2]. In addition, several industrial plants produce large amounts of wastewater containing high concentration of phthalates causing a negative impact on the aquatic environment. Due to their large scale industrial production and wide domestic utilization, they are ubiquitous in the environment [3,4]. Because of their very large production amounts and use, and their toxicity, it seems very important to develop processes able to

---

* Corresponding author.

eliminate these pollutants from contaminated water. The most commonly used method for removal of phthalates from wastewater is the biological treatment, based on the metabolic degradation of phthalates by micro-organisms under aerobic [5] or anaerobic [6] conditions. However, several studies reported that phthalates acid esters with long alkyl-chains are poorly degraded [7] and some of them are considered recalcitrant to biological treatment [8]. On the other hand, the advanced oxidation processes (AOPs) are considered as promising environmentally friendly technologies for the treatment of wastewaters containing low contents of persistent organic pollutants (POPs) [9–16]. AOPs include a large variety of chemical, photochemical, photocatalytic and direct and indirect electrochemical methods characterized by the in situ generation of hydroxyl radical ($^\bullet$OH) which is the second most strong oxidizing species known after fluorine. This radical has a very high oxidation power ($E_0(^\bullet OH/H_2O)$ = 2.80 V vs. *SHE*) and thus is able to non-selectively react with POPs to yield dehydrogenated or hydroxylated derivatives that can in turn undergo reactions with $^\bullet$OH until overall mineralization, i.e., total conversion into CO_2 and H_2O.

The Fenton process is recognized as one of the most powerful advanced oxidation technologies available and can be used to destroy a variety of recalcitrant organic pollutants. Hydroxyl radicals are produced from Fenton's reagent, a mixture of H_2O_2 and ferrous ions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \qquad (1)$$

The treatment of polluted effluents by this system require the use of important amount of Fenton's reagent (mixture Fe(II) + H_2O_2) and produce $Fe(OH)_3$ sludge. The process can be catalysed in excess of H_2O_2 [Reactions (2),(3)] but this catalysis is very slow and may not prevent the accumulation of Fe(III) and consequently the formation of the process sludge.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \qquad (2)$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \qquad (3)$$

Another drawback of this system is the involvement of the following waste reaction [Reaction (4)] in the presence of high Fe(II) concentrations which reduces the process efficiency.

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + HO^- \quad k = 7.5 \times 10^9\ M^{-1}s^{-1} \qquad (4)$$

Reaction (4) may adversely affect the efficiency of the classical Fenton process in particular with high ferrous ion concentrations. To eliminate some drawbacks of this process and enhance its efficiency dark Fenton process, the so-called photo-Fenton process, which consist in photocatalysis of the Fenton's reaction, has been developed. The photoreduction of $Fe(OH)^{2+}$, which is the predominating Fe(III) species at pH 3.0, according to Reaction (5) leads to the continuous regeneration of Fe2+ thus catalyzing Fenton's [Reaction (1)] [17] on the one hand and produces additional hydroxyl radicals [18–20] on the other:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH \qquad (5)$$

Unlike the dark Fenton process, the photo-Fenton process use a catalytical amount of an iron salt and can be conducted using Fe(II) or Fe(III) species as catalyst. In fact, the combination of Fe^{3+} in the presence of the excess of H_2O_2 (Fenton-like process) leads to in situ generation of Fe^{2+} through Reaction (2) [21–23], which reconstitutes the Fenton's reagent (with the excess of H_2O_2).

In addition, the UV light irradiation of the solution can induce the photodegradation of some oxidation by-products and enhance the mineralization efficiency by breakdown of the complexes of carboxylic acids with Fe(III) which are recalcitrant to AOPs. This is the case of the photodecarboxylation of Fe(III) carboxylate species according to Reaction (6). This reaction promoting Fe^{2+} regeneration, contributes also to the catalysis of the Fenton's reaction:

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^\bullet \qquad (6)$$

For example, oxalic acid forms complexes such as $Fe(C_2O_4)^+$, $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_{33}^-$ that absorb photons in the range 250–580 nm and whose photodecarboxylation follows Reaction (7) by passing through an excitation state undergoing a ligand–metal charge transfer:

$$2Fe(C_2O_4)_n^{(3-2n)} + h\nu \rightarrow 2Fe^{2+} + (2n-1)C_2O_4^{2-} + 2CO_2 \qquad (7)$$

The UV irradiation of the solution can also produce hydroxyl from photolysis of H_2O_2 present in the medium by its homolytic breaking [24]:

$$H_2O_2 + h\nu \rightarrow 2\,{}^\bullet OH \qquad (8)$$

Thus in the photo-Fenton process the chemical and photochemical reactions [Reactions (1), (5) and (8) respectively] contribute to the formation of a high amount of hydroxyl radicals and thus enhance the degradation rate of organic pollutants. Therefore, the photo-Fenton process is regarded as an effective approach for the degradation of recalcitrant organic pollutants [24].

The application of the photo-Fenton process to the oxidation of the phthalic anhydride has been reported in this work. We aimed to determine the influence of some experimental parameters governing the oxidation. Thereafter, the mineralization of a synthetic phthalic anhydride solution was achieved under the optimal conditions.

2. Materials and methods

2.1. Chemicals

Phthalic anhydride (purity 97%) and H_2O_2 (30% w/w) were obtained from Fluka. Concentrated H_2SO_4 (96%) used to adjust solution pH to 3 and Iron (III) sulphate pentahydrate (analytical grade) used as Fe^{3+} (catalyst) source were obtained from Acros. Solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system with resistivity > 18 MΩ cm at room temperature.

2.2. Photochemical cell and analytic apparatus

The mineralization process of phthalate solutions by photo-Fenton process ($Fe^{3+}/H_2O_2/UV$) was performed in a Pyrex batch annular photoreactor (described in [21]) of 1.3 L equipped with a low pressure mercury vapour lamp (Heraeus NNI-Noblelight 40/20) operating near room temperature. The UV-lamp nominal power was 12 W (rated power being 40 W) and the photon flow entering the reactor was 11.2×10^{-6} Einstein s^{-1}. It was protected from the solution by a quartz tube placed in axial position. The photoreactor comprises a double wall for circulating cooling water. The solution was circulated through the reactor by a membrane pump (KNF Neuberger with a flow of 3 L min^{-1}) in order of its homogenization. The adequate amounts of H_2O_2 and Fe^{3+} were introduced into the photoreactor just before turning the UV lamp. The reactor was covered by an aluminium film before switching on the lamp to avoid the UV radiation, on the one hand, and avoid any reaction involving sunlight, on the other hand.

The mineralization efficiency of treated solutions was monitored by the abatement of the total organic carbon (TOC) using a Shimadzu VCSH TOC analyser. Samples were withdrawn from the treated solution at different treatment times before analysis. Reproducible TOC values with ±2% accuracy were found using the non-purgeable organic carbon method.

The decay kinetics of phtalic anhydride concentration was followed by reversed-phase HPLC using a Merck Lachrom liquid chromatograph equipped with a L-7100 pump, fitted with a Purospher RP-18 5 μm, 25 cm × 4.6 mm (i.d.) column at 35°C using a methanol–water mixture as mobile phase at 0.8 mL s^{-1}.

The identification and quantification of oxalic acid was carried out by ion-exclusion HPLC chromatography using the same HPLC system fitted with a Supelcogel H 9 μm, 25 cm × 4.6 mm (i.d.) column at room temperature, selecting UV detector at $\lambda = 220$ nm. A 0.1% H_3PO_4 solution at a flow rate of 0.5 mL min^{-1} was used as the mobile phase.

3. Results and discussion

3.1. Influence of the ratio R = *$[H_2O_2]/[Fe^{3+}]$ on the mineralization efficiency*

A blank experiment aiming to assess the contribution of direct photolysis of phtalic anhydride was carried out in the absence of H_2O_2 and Fe^{3+}. This experiment showed that UV photons have a very slow and then negligible action on the phtalic anhydride degradation. Thus the effect of ratio *R* was studied by photo-Fenton treatment. Fig. 1 shows the evolution of the solution TOC during the mineralization of aqueous solution of phthalic anhydride ($C_0 = 0.2$ mM) in function of the irradiation time for different values of the ratio *R* in the range 10–60 at a fixed Fe^{3+} initial concentration of 0.1 mM. Results obtained show that the solution TOC decay kinetics increases by increasing the *R* value. The mineralization degree (in terms of TOC abatement) of phthalic anhydride solution increases quickly in the range of *R* from 10 to 40 from 77% to 91% after 1 h of treatment. A TOC removal efficiency of 98.7% indicating an almost complete mineralization of the solution was obtained for the ratio $R = 40$ after 6 h of treatment. This very high mineralization efficiency compared to the classical Fenton process (data not showed) can be explained thanks to the generation of a great amount of hydroxyl radicals according to Reactions (1), (5) and (8) during the photo-Fenton process. Reaction (6) which favours the mineralization of short chain carboxylic acids by photochemical breaking of their complexes with Fe(III) contributes also significantly to the enhancement of the mineralization efficiency .

The *R* values up to 40 lead to a weakening in mineralization kinetics because H_2O_2 behaves as hydroxyl radical scavenger following Reactions (9), (10) at high concentrations [24–26] and thus constitute a limiting factor of the mineralization degree.

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2^\bullet + H_2O \tag{9}$$

$$HO_2^\bullet + {}^\bullet OH \rightarrow H_2O + O_2 \tag{10}$$

This experimental result was also confirmed by determination of apparent rate constant between phtalic anhy-

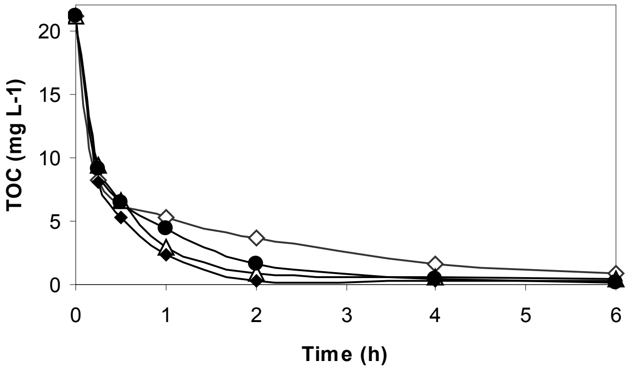

Fig. 1. Effect of the ratio $R = [H_2O_2]/[Fe^{3+}]$ on the TOC removal kinetics of phthalic anhydride aqueous solution during photo-Fenton treatment. *R*: 10 (◊); 20 (Δ); 40 (♦) and 60 (●). Experimental conditions: $[\text{phthalic anhydride}]_0 = 0.2$ mM, $[Fe^{3+}] = 0.1$ mM, pH = 3, $V = 1.3$ L.

dride and hydroxyl radicals. Indeed the kinetic decay of phtalic anhydride concentration in function of irradiation time is indicating the oxidation of phtalic anhydride by hydroxyl radical can be described by pseudo-first order reaction kinetics (assuming a quasi-stationary state for hydroxyl radical concentration). Corresponding apparent rate constants (k_{app}) were than determined from linear regression of the pseudo first order kinetic model [ln (C_0/C_t) = $f(t)$] fitting enough well ($R^2 > 0.983$). Fig. 2 shows the evolution of k_{app} as a function of R and shows that it gradually increases in the range of $10 > R > 40$, optimum kinetics being attained at $R = 40$.

Consequently $R = 40$ was chosen as optimal value for Fe(III) initial concentration of 0.2 mM in photo-Fenton treatment of phtalic anhydride aqueous solutions.

3.2. *Influence of Fe^{3+} initial concentration*

The concentration of Fe^{3+} (as catalyst) constitutes another important parameter of the photo-Fenton process. To determine the effect of Fe^{3+} concentration on the oxidative degradation of phthalic anhydride, several experiments were carried out in acidic solutions of pH 3 at constant concentration of phthalic anhydride (C_0 = 0.2 mM) and at room temperature, varying Fe^{3+} initial concentration in the range 0.0–0.2 mM (Fig. 3) at an optimal R value obtained above. It can be seen from Fig. 3 that the use of hydrogen peroxide alone is also able to conduct the overall mineralization of phthalic anhydride solution due to the very effective H_2O_2 photolysis quantum yield at 253.7 nm from Reaction (8). However this system requires a long irradiation time because of the low absorption coefficient and consequently the slow mineralization kinetics resulting from the photolysis of H_2O_2 [Reaction (8)].

On the other hand, the phthalic anhydride removal rate (in terms of TOC abatement) increases with the increase of catalyst concentration. Indeed, it passes from 21 to 91% after 1 h of treatment corresponding to the increase of ferric ions concentration from 0.0 to 0.1 mM and leading to overall mineralization at 2 h of treatment. This great oxidation power of the photo-Fenton process can be accounted for by the high amount of ·OH simultaneously generated from Reactions (1), (3) and (8).

Further increase up to 0.1 mM in Fe^{3+} concentration leads to a decrease of the mineralization efficiency due to enhancement of the wasting parasitic Reaction (4) which becomes competitive for hydroxyl radicals thus leading to the weakness of the oxidation reaction of phtalic anhydride. An excess of iron ions may be detrimental to the overall reaction since the oversupplied Fe^{3+} yields Fe^{2+} according to Reaction (2) maximizing the percentage of scavenged hydroxyl radicals through Reaction (4) [27] with $k = 3 \times 10^8$ M^{-1} s^{-1} [23]. This condition can also cause the recombination of hydroxyl radicals [28].

Consequently, the value of 0.1 mM has been selected as optimal catalyst concentration for following experiments.

3.3. *Mineralization of phthalic anhydride under optimum conditions*

The mineralization of phthalic anhydride aqueous solution with hydroxyl radicals generated by the photo-Fenton process was studied under optimal conditions determined above, i.e. R ($[H_2O_2]/[Fe^{3+}]$) = 40 and $[Fe^{3+}]$ = 0.1 mM. Fig. 4 shows the evolution of solution TOC during the treatment. Mineralization kinetics is very fast at the beginning of the process with an exponential decrease of the solution TOC. TOC abatement efficiency was 50, 80 and 92% for 15, 30 and 60 min respectively.

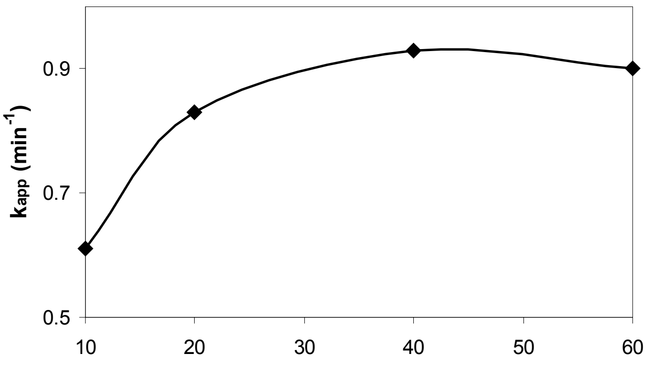

Fig. 2. Evolution of the apparent rate constant (k_{app}) for the oxidation of the phthalic anhydride in function of R during photo-Fenton treatment. Experimental conditions: [phthalic anhydride]$_0$ = 0.2 mM, $[Fe^{3+}]$ = 0.1 mM, pH = 3.

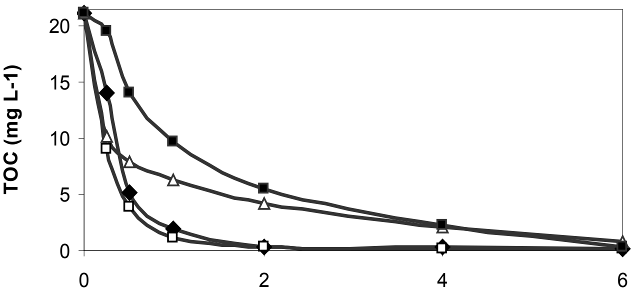

Fig. 3. Effect of the catalyst (Fe^{3+}) concentration on the TOC removal (as a mineralization parameter) of phthalic anhydride aqueous solution as a function of treatment time during photo-Fenton treatment. $[Fe^{3+}]$: 0 (■); 0.05 (♦); 0.1 (□) and 0.2 (Δ). Experimental conditions: [phthalic anhydride]$_0$ = 0.2 mM, R = 40, pH = 3, V = 1.3 L.

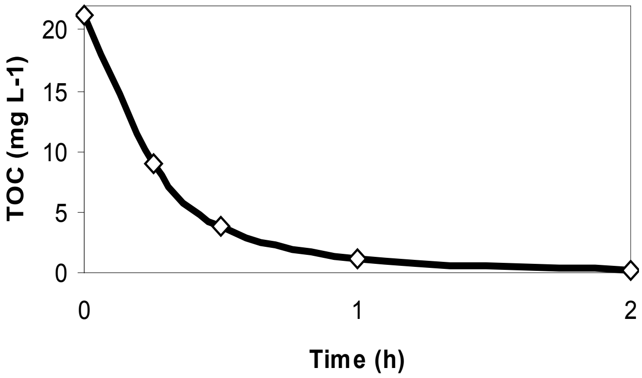

Fig. 4. TOC abatement evolution during the mineralization of phthalic anhydride aqueous solution by photo-Fenton process under optimum conditions. [phthalic anhydride]$_0$ = 0.2 mM, R = 40, [Fe^{3+}] = 0.1 mM, pH = 3, V = 1.3 L.

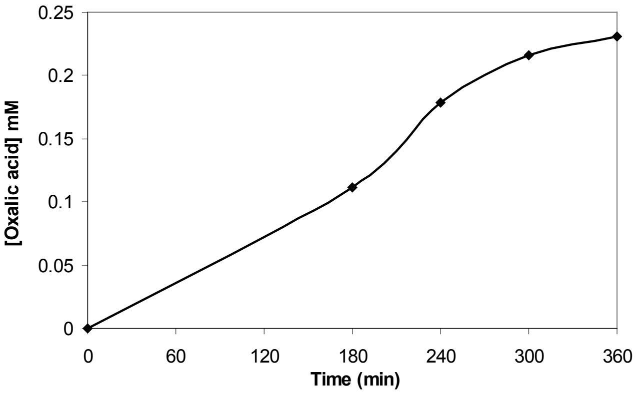

Fig. 5. Evolution of the oxalic acid concentration during dark Fenton treatment of phthalic anhydride aqueous solution under optimum conditions: [phthalic anhydride]$_0$ = 0.2 mM, R = 40, [Fe^{3+}] = 0.1 mM, pH = 3, V = 1.3 L.

The overall mineralization (98.7% TOC abatement) was reached after only 2 h of photo-Fenton treatment. This result highlights the great mineralization ability of the photo-Fenton process. The great mineralization power of this process can be explained by the simultaneous production of hydroxyl radicals pointed out above, but also by the role of photodecarboxylation Reactions (6) and (7) which facilitate the mineralization of aliphatic carboxylic acids by promoting the breakdown of its stable complexes with Fe(III).

3.4. Influence of UV irradiation on the mineralization efficiency

It is well known that the AOPs generate short-chain carboxylic acids which have poor reaction rates with hydroxyl radicals [9,17,20,28–30]. In the case of the presence of Fe^{3+} mineralization becomes more difficult due to the formation of stable Fe(III)–carboxylic acid complexes. This is particularly the case of oxalic acid which persists for longer time of treatment. Flox et al. [29,30] reported that UV irradiation of the solution enhances the mineralization efficiency according to Reactions (6) and (7) through breaking of these complexes by photoreduction of Fe(III).

To assess the effect of UV irradiation on the mineralization of phtalic anhydride solution we carried out the dark Fenton treatment under the same experimental conditions in order to follow the formation and evolution of oxalic acid which is the most commonly formed carboxylic acid during AOPs treatment. The results depicted in Fig. 5 show that oxalic acid is hardly oxidized in the dark Fenton process and accumulated in the solution. Its concentration reached 0.23 mM at 6 h of treatment. On the other hand, under the same experimental conditions but with UV irradiation (photo-Fenton) oxalic acid concentration remained very poor and disappeared completely after a treatment time of 2 h. This very fast oxalic acid in the presence of UV light irradiation highlights the enhancement of the mineralization leading to a TOC decay of 98.7% and can be accounted for by the involvement of photodecarboxylation Reactions (6) and (7).

4. Conclusion

The photo-Fenton process was used to produce hydroxyl radicals in order to oxidize phtalic anhydride in aqueous medium until its mineralization. The effect of ratio $R = [H_2O_2]/[Fe^{3+}]$ and the catalyst concentration on the mineralization efficiency were studied and the optimal conditions of ratio R = 40 and [Fe^{3+}] = 0.1 mM were found for phtalic anhydride mineralization. The overall mineralization (98.7% TOC removal) of 0.2 mM phthalic anhydride aqueous solution was obtained after only 2 h of photo-Fenton treatment under optimal operating conditions. The positive effect of UV light irradiation on the enhancement of the mineralization effectiveness was also demonstrated.

References

[1] F. Alatriste-Mondragon, R. Iranpour and B.K. Ahring, Toxicity of di-(2-ethylhexyl) phthalate on the anaerobic digestion of wastewater sludge, Wat. Res., 37 (2003) 1260–1269.
[2] A. Marcilla, S. García and J.C. García-Quesada, Study of the migration of PVC plasticizers, J. Anal. Appl. Pyrol., 71 (2004) 457–463.
[3] M. Clara, G. Windhofer, W. Hartl, K. Braun, M. Simon, O. Gans, C. Scheffknecht and A. Chovanec, Occurrence of phthalates in surface runoff, untreated and treated wastewater and fate during wastewater treatment, Chemosphere. 78 (2010) 1078–1084.
[4] C. Dargnat, M.-J. Teil, M. Chevreuil and M. Blanchard, Phthalate removal throughout wastewater treatment plant: Case study of Marne Aval station (France), Sci. Total Environ., 407 (2009) 1235–1244.
[5] N. Scholz, R. Diefenbach, I. Rademacher and D. Linneman,

Biodegradation of DEHP, DBP, and DINP: Poorly water soluble and widely used phthalate plasticizers, B. Environ. Contam. Tox., 58 (1997) 527–534.

[6] [W. Jianlong, C. Lujun, S. Hanchang and Q. Yi, Microbial degradation of phthalic acid esters under anaerobic digestion of sludge, Chemosphere, 41 (2000) 1245–1248.

[7] J. Ejlertsson, M. Alnervik, S. Jonsson and B.H. Svesson, Influence of water solubility, side-chain degradability, and side-chain structure on the degradation of phthalic acid ssters under methanogenic conditions, Environ. Sci. Technol., 31 (1997) 2761–2764.

[8] A.M. Saillenfait and A. Laudet-Hesbert, Phtalates (II), EMC-Toxicol,-Pathol., 2 (2005) 137–150.

[9] S. Hammami, N. Bellakhal, N. Oturan, M.A. Oturan and M. Dachraoui, Degradation of Acid Orange 7 by electrochemically generated $^{\bullet}$OH radicals in acidic aqueous medium using a boron-doped diamond or platinum anode: A mechanistic study, Chemosphere, 73 (2008) 678–684.

[10] A. Kesraoui Abdessalem, N. Oturan, N. Bellakhal, M. Dachraoui and M.A. Oturan, Experimental design methodology applied to electro-Fenton treatment for degradation of herbicide chlortoluron, Appl. Catal. B: Environ., 78 (2008) 334–341.

[11] M.A Oturan, M.C. Edelahi, N. Oturan, K. El Kacemi and J.J. Aaron, Kinetics of oxidative degradation/mineralization pathways of the phenylurea herbicides diuron, monuron and fenuron in water during application of the electro-Fenton process, Appl. Catal. B: Environ., 97 (2010) 82–89.

[12] S. Trabelsi, N. Oturan, N. Bellakhal and M.A. Oturan, Electrochemical oxidation of ohthalic anhydride in aqueous medium by electro-Fenton process, J. Environ. Eng. Manage., 19 (2009) 291–297.

[13] E. Guinea, J.A. Garrido, R.M Rodríguez, P.L Cabot, C. Arias, F. Centellas and E. Brillas, Degradation of the fluoroquinolone enrofloxacin by electrochemical advanced oxidation processes based on hydrogen peroxide electrogeneration, Electrochim. Acta, 55 (2010) 2101–2115.

[14] M. Skoumal, R.M. Rodríguez, P.L Cabot, F.Centellas, J.A. Garrido, C. Arias and E. Brillas, Electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton degradation of the drug ibuprofen in acid aqueous medium using platinum and boron-doped diamond anodes, Electrochim. Acta, 54 (2009) 2077–2085.

[15] M.A Oturan, J. Bizot, D. Deprez and B. Terlain, Reaction of inflammation inhibitors with chemically and electrochemically generated hydroxyl radicals, J. Electroanal. Chem., 334 (1992) 103–109.

[16] B. Utset, J. Garcia, J. Casado, X. Domènech and J. Peral, Replacement of H_2O_2 by O_2 in Fenton and photo-Fenton reactions, Chemosphere, 41 (2000) 1187–1192.

[17] J.J. Pignatello and Y. Sun, Complete oxidation of metolachlor and methyl parathion in water by the photoassisted Fenton reaction, Wat. Res., 29 (1995) 1837–1844.

[18] F. Fdil, J.J. Aaron, N. Oturan, A. Chaouch and M.A. Oturan, Dégradation photochimique d'herbicides chlorophenoxyalcanoïques en milieux aqueux, Rev. Sci. Eau, 16 (2003) 123–142.

[19] G. Kaichouh, N. Oturan, M.A. Oturan, A. El Hourch and K. El Kacemi, Mineralization of herbicides imazapyr and imazaquin in aqueous medium by, Fenton, photo-Fenton and électro-Fenton processes, Environ. Technol., 29 (2008) 489–496.

[20] E. Brillas, I. Sires and M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, Chem. Rev., 109 (2009) 6570–6631.

[21] M. Diagne, N. Oturan, M.A. Oturan and I Sirés, UV-C light-enhanced photo-Fenton oxidation of methyl parathion, Environ. Chem. Lett., 7 (2009) 261–265.

[22] W. Chu, C.Y. Kwan, K.H. Chan and S.K. Kam, A study of kinetic modelling and reaction pathway of 2,4-dichlorophenol transformation by photo-Fenton-like oxidation, J. Hazard. Mater. B, 121 (2005) 119–126.

[23] J. De Laat, H. Gallard, S. Ancelin and B. Legube, Comparative study of the oxidation of atrazine and acetone by H_2O_2/UV, Fe(III)/UV, Fe(III)/H_2O_2/UV and Fe(II) or Fe(III)/H_2O_2. Chemosphere, 39 (1999) 2693–2706.

[24] J.H. Baxendale and J.A. Wilson, The photolysis of hydrogen peroxide at high light intensities, Trans. Faraday Soc., 53 (1957) 344–356.

[25] I. Peternel, N. Koprivanac and H. Kusic, UV-based processes for reactive azo dye mineralization, Wat. Res., 40 (2006) 525–532.

[26] M. Tokumura, H.T. Znad and Y. Kawase, Decolorization of dark brown colored coffee effluent by solar photo-Fenton reaction: Effect of solar light dose on decolorization kinetics, Wat. Res., 42 (2008) 4665–4673.

[27] M.Y. Ghaly, G. Härtel, R. Mayer and R. Haseneder, Photochemical oxidation of p-chlorophenol by UV/H_2O_2 and photo-Fenton process. A comparative study, Waste Manage.. 21 (2001) 41–47.

[28] [28] C.S. Chiou, Application of steel waste with UV/H_2O_2 to mineralize 2-naphthalenesulfonate in aqueous solution, Separ. Purif. Technol. 55 (2007), pp.110–116.

[29] A. Serra, X. Domènech, C. Arias, E. Brillas and J. Peral, Oxidation of α-methylphenylglycine under Fenton and electro-Fenton conditions in the dark and in the presence of solar light, Appl. Catal. B: Environ., 89 (2009) 12–21.

[30] C. Flox, J.A. Garrido, R.M. Rodríguez, P.L Cabot, F. Centellas, C. Arias and E. Brillas, Mineralization of herbicide mecoprop by photoelectro-Fenton with UVA and solar light, Catal. Today. 129 (2007) 29–36.

[31] C. Flox, P.L. Cabot, F. Centellas, J.A Garrido, R. M Rodríguez, C. Arias and E. Brillas, Solar photoelectro-Fenton degradation of cresols using a flow reactor with a boron-doped diamond anode, Appl. Catal. B: Environ., 75 (2007) 17–28.