Fetah I. PODVORICA*

ADVANCED OXIDATION PROCESSES FOR THE DEGRADATION OF PERSISTENT ORGANIC POLLUTANTS IN WATER

Abstract: The need for fresh drinking water is increasing in the world and according to the World Health Organization data, about 80 % of diseases that affect the population are due to the use of contaminated water. Persistent organic pollutants (POPs) molecules are very stable synthetic chemicals produced for different purposes: pesticides, industrial processes, by-products and medicaments etc. They are released into soil, water and air and due to their high stability they may enter the food-chain. The presence of POPs and other toxic pollutants into water compartments may cause harmful effects for humans and animals therefore there are needed strict regulations about the release of these chemicals. The use of conventional methods like biological processes, chemical coagulation, membrane filtration, adsorption is not suitable for their complete removal from contaminated soils, water and wastewater plants.

Advanced oxidation processes (AOPs) involve the production of a very strong oxidizing agent, the hydroxyl radicals that are very useful agents capable to completely mineralize organic pollutants into carbon dioxide, water and inorganic ions. Hydroxyl radicals can be generated from hydrogen peroxide by various methods like heterogeneous and homogeneous photocatalysis based on UV and solar irradiation, ozonation, Fenton and Electro-Fenton process. These methods permit the efficient degradation of the POPs and the new technologies based on electrochemical advanced processes are going to pass from academic research level to large-scale treatments.

Key words: *Persistent Organic Pollutants, Drinking Water, Advanced Oxidation Processes, hydroxyl radical*

* Academy of Sciences and Arts of Kosovo

1. INTRODUCTION

The development of the world chemical industry during the last decades enabled the production of numerous chemical compounds such as polymers; composite materials, pesticides, colorants, pharmaceuticals etc. that have served for many purposes and have greatly increased the productivity in agriculture. Despite their positive impact for specific tasks their presence in the environment represents also a danger for the living organisms. Those chemicals are spread in the environment after their use in many ways and are concentrated in different places by different transport ways: air, water and soil. Some of these products are removed and eliminated by classical conventional physico-chemical methods but there are also some organic compounds persist to standard treatment processes and their total degradation can takes many decades or centuries. The chemical compounds which are very resistant to different chemical or biological agents are called persistent organic pollutants. As part of this category are considered pesticides like Aldrin, Dieldrin, Chlorodane, DDT (Dichlorodiphenyltrichloroethane), Endrin, Heptachlor, Mirex and Toxaphene; industrial chlorinated chemicals known as polychlorobiphenyls or PCBs and dibenzodioxins and Dibenzofurans. Although the use of some of these chemicals is banned since several decades, [1] they are still released into the environment from many sources as those materials have been used for many purposes. Due to their high stability, volatility and low water solubility they may be transported to long distances as they are recycled between air, water and soil. [2] Those chemicals may have the affinity to interact with the leaves and food crops and after the consumption of contaminated food they enter into the human bodies they may affect their health in different ways. POPs are considered to cause diabetes, endocrine disturbance, cancer, cardiovascular and reproductive problems. [3]

Another major concern today for the world population is the production of fresh drinking water for all inhabitants. Despite its omnipresence on Earth, about 70% of the terrestrial area is covered with water but it is constituted by aquatic resources that are not directly used by human beings like salted waters of seas and oceans and glaciers. It remains only a very small portion about 0.65 % of water that can be utilized for drinking without further treatment if there is not any kind of pollution. These sources of water are not equally spread over the world. Human activities in many areas such industry, agriculture, transport, medicine, construction etc. have largely contributed to underground and surface water pollution with many toxic compounds. Human population is growing very fast and therefore is really important to develop very efficient methods for the removal of pollutants from the contaminated waters. [4] World Health Organization has published data which stipulates that about 80 % of diseases that affect the population are due to the use of contaminated water. [5]

There exist many physico-chemical conventional methods the so-called non-destructive separation techniques that remove the pollutants from water and concentrate them into another phase such as: decantation, adsorption, extraction, coagulation, membrane filtration etc. Destructive methods use very powerful chemical oxidation agents which enable the chemical transformation of the toxic compounds into their final products carbon dioxide and water and include biological, thermal and chemical methods. Biological methods such bioremediation use different microorganisms as agents to convert toxic organic molecules into CO_2, methane, water and inorganic compounds. These transformations are not very fast, it may take months under aerobic and anaerobic conditions as in the case of the pharmaceutical product naproxen [6], there are some pH and other limitations like the presence of membrane fouling with toxic sludge and some chemicals withstand to this treatment. [7]

The thermal treatment or incineration method consists on the burning of the organic compounds and their transformation into CO_2, water and ash and the heat is released.

A detailed review of abovementioned methods used for the removal of organic pollutants during the water treatment may be found elsewhere, see for example [8] while in this paper the main focus will be on the basic principles of advanced oxidation processes.

2. ADVANCED OXIDATION PROCESSES

The concept advanced oxidation processes is used for all water depollution treatment processes made in normal conditions near ambient temperature and pressure. [9] The common point of all these processes is the *in situ* formation of hydroxyl radical, OH, by different ways: chemically, photochemically or electrochemically, as is seen in the Figure 1. This radical is the most powerful oxidation agent after the fluorine, it is very unstable and those radicals react steadily with organic molecules in chain reactions and transform them as final products into CO_2 and water. Its oxidation potential is $E° = 2.80$ V/SHE, SHE-standard hydrogen electrode and compared with ozone, its reactivity toward organic compounds is usually several orders of magnitude higher than that of ozone under same conditions. This higher reactivity is due to fact that the hydroxyl radical contains unpaired electron while ozone and hydrogen peroxide have paired electrons in their

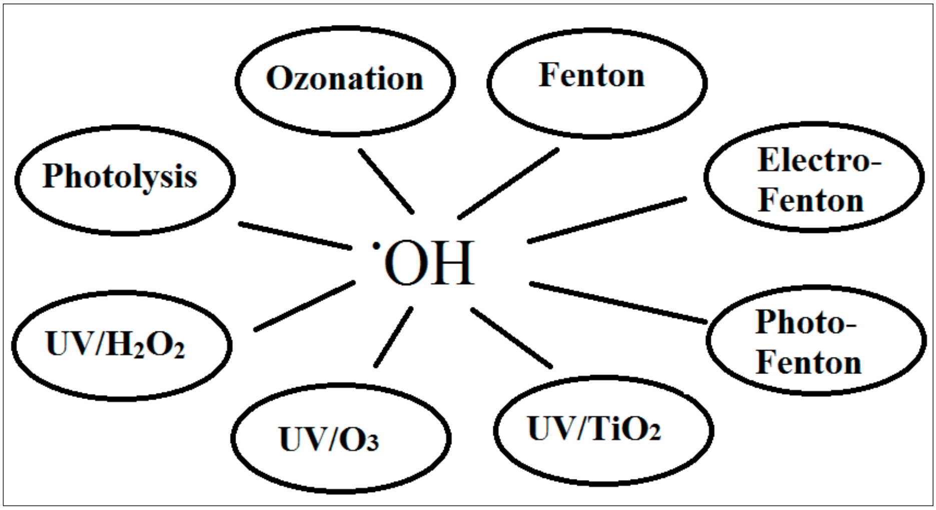

Fig. 1. Different advanced oxidation processes that produce hydroxyl radicals

molecules. Hydroxyl radicals are able to destroy completely organic pollutants by abstraction of hydrogen atoms from their hydrocarbon chains or by attacking unsatured bonds in alkenes, dienes or aromatic ring.

3. OZONATION

Ozone molecule is a strong oxidant and in aqueous solutions at aqueous basic solutions enables the formation of hydroxyl radicals according to the following reactions:

$$O_3 + {}^{-}OH \rightarrow O_2^{-} + HO_2$$
$$O_2^{-} + O_3 \rightarrow O_3^{-} + O_2$$
$$O_3^{-} + H+ \rightarrow HO_3$$
$$HO_3 \rightarrow {}^{\cdot}OH + O_2$$

The treatment with ozone is very appropriate for wastewaters that contain POPs and inorganic ions of sulfides and cyanides at high pH values. The use of other AOPs that operate at lower pH values will increase the risk of release of highly toxic gases H_2S and HCN.

The mixture of ozone and hydrogen peroxide is one of the most used for water treatment. H_2O_2 is deprotonated in aqueous solution according to the reaction:

$$H_2O_2 + H_2O \rightarrow HO_2^{-} + H_3O^{+}$$

The creation of hydroxyl radicals is enhanced when ozone reacts with the deprotonated hydrogen peroxide by this reaction:

$$O_3 + HO_2^- \rightarrow O_2 + {}^{\cdot}OH + HO_2^{-\cdot}$$

Therefore the combination of ozone and hydrogen peroxide makes possible the removal of persistent organic pollutants including POPs from water after a short time treatment. [10] It improves the degradation rate of organic pollutants and has a very high bactericide activity, is quite simple to hand and always is used in the disinfection of drinkable waters. The main disadvantage of this process is the cost of all treatment and sometimes it is coupled with other costless methods.

4. HOMOGENEOUS PHOTOLYSIS OF HYDROGEN PEROXIDE

UV/H_2O_2 treatment. UV radiation with wavelength < 300 nm has enough energy to transform the hydrogen peroxide molecule into hydroxyl radicals according to the reaction:

$$H_2O_2 + hn \rightarrow 2\,{}^{\cdot}OH$$

These radicals generated via the H_2O_2 photolysis undergo further nonspecific reactions with other organic molecules and transform them into nontoxic molecules. [11]

UV/O_3 treatment. Irradiation of ozone molecule in the presence of water with a mercury lamp that enables UV radiation at the 254 nm permits the formation of hydroxyl radicals according to the reaction:

$$O_3 + H_2O + hn \rightarrow 2\,{}^{\cdot}OH + O_2$$

These photolysis methods are useful for the complete oxidation of different organic compounds in waste water treatment like drugs, benzene and its derivatives, volatile chlorinated organic compounds etc. [12]

5. HETEROGENEOUS PHOTOCATALYSIS

TiO_2/UV treatment. Titanium dioxide is a semiconductor that under irradiation of UV light serves as heterogeneous photo catalyst because of its affinity to generate oxidation-reduction reactions. [13] The reason for such behavior is that the absorbed photons have enough energy to promote the move of the electron from the valence to the conducting band of the semiconductor and an electron-hole pair is formed as is shown in the following reaction:

$$TiO_2 + hn \rightarrow e- + h^+$$

If this electron-hole pair is not recombined, it can induce redox reactions on the surface of the catalyst as it is the case with the water molecule which is transformed into hydrogen and oxygen. The photo-generated holes are very strong oxidants and either oxidize directly organic molecules either oxidize the hydroxide ions to hydroxyl radicals which in their turn make the indirect oxidation of these compounds. [14]

$$TiO_2\ (h^+) + OH^-_{(ads)} \rightarrow TiO_2 + {}^{\cdot}OH$$

Although there exist other semiconductor metal oxide as photocatalysts, the TiO_2 is used at great extent due to its physico-chemical characteristics: chemical inertness, non-toxicity, photoactivity and low cost. Heterogeneous photocatalysis has shown high performance for the total mineralization of many POPs such pesticides [15] and pharmaceuticals [16].

6. FENTON REACTION

Fenton has discovered at the end of the XIX century that iron (II) ions react with hydrogen peroxide in aqueous acid solution and form hydroxyl radicals through the reaction:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\cdot}OH + H_2O$$

This reaction is driven with a small amount of iron (II) ions because at pH 3 these ions are regenerated when the iron (III) ions are reduced from the so-called Fenton-like reaction:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+$$
$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+$$

When the quantity of Fe_2 + ions is very high they react with produced ${}^{\cdot}OH$ therefore the concentration of iron salt must be controlled in order to prevent the unwanted consumption of hydroxyl radicals. [17] For continuous use of Fenton process in wastewater treatment it is necessary to have a fixed concentration ratio of catalyzer (Fe^{2+} ions) and H_2O_2.

The main advantages of such process are: easy implementation of the method and easy handling of the chemicals because hydrogen peroxide is considered as green chemical because when it is decomposed gives rise to water and oxygen as by products. It has however several disadvantages:

Relatively high cost of the used chemicals for the process and the maintenance of the nearly constant pH, the transportation and the storage of hydrogen peroxide represents some risks, deposition and accumulation of high quantity of iron sludge during the process.

7. ELECTRO-FENTON PROCESS

Electrochemistry is a powerful technique based on the electron transfer that makes possible many oxidation and reduction reactions. A great improvement of Fenton process is achieved with the use of electrochemistry to assist the regeneration of iron (II) ions and the formation of hydrogen peroxide during the electrochemical reduction of oxygen in the cathode surface. The electrochemical generation of H_2O_2 from the dissolved oxygen molecules in aqueous acid solution is a two electron reduction process and is given in the following reaction:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

In situ produced hydrogen peroxide reacts immediately with iron (II) ions and produces hydroxyl radicals, Fenton reaction, while the iron (III) ions created as products of this process are simultaneously electrochemically reduced at the cathode and enable to regenerate the iron (II) ions:

$$Fe^{3+} + 1\ e^- \rightarrow Fe^{2+}$$

The big advantage of electro-Fenton process is the continuous production of H_2O_2 from air oxygen dissolved in water and regeneration of iron (II) ions at the cathode that allow the formation of hydroxyl radicals in a permanent way. These radicals, in the presence of organic pollutants, react immediately with and transform them into final carbon dioxide and water.

The scheme of the reactor for the electro-Fenton process is shown in the Figure 2. A power supply is used to impose to the electrodes a potential difference that is sufficient to drive the electrochemical reactions of the oxygen reduction into hydrogen peroxide and iron (III) reduction into iron (II). The quantity of the oxygen needed for the hydrogen peroxide production is furnished from the compressed air. As cathode materials are used different carbon types, especially carbon felt electrodes because they have a high specific surface that provides higher rate for the production of the hydrogen peroxide during the oxygen electrochemical reduction and are low cost. The potential of the cathode must be well controlled because the imposition of high negative potential enables two side reactions: the reduction of oxygen molecule into water and the hydrogen evolution reaction form the protons in aqueous acid solution:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
$$2H^+ + 2e^- \rightarrow H_2$$

The composition of anode material is also very important due to the ability of certain anodes when are biased under a high positive potential are able to produce a high quantity of hydroxyl radicals via water molecule oxidation according to the reaction:

$$M + H_2O \rightarrow M(^{\cdot}OH) + H^+ + 1\ e^-$$

where M and M($^{\cdot}$OH) represent the anode material and hydroxyl radicals adsorbed on the anode surface respectively. [18] Many materials are tested as anode materials and the best performances have shown so-called boron doped diamond electrode that enables a very efficient total degradation of persistent organic pollutants in the combination with carbon cathode. [19] It has a high capacity to produce a larger quantity of hydroxyl radicals and in the combination with hydroxyl radicals produced during the electro-Fenton process leads to a fast and complete removal of organic pollutants.

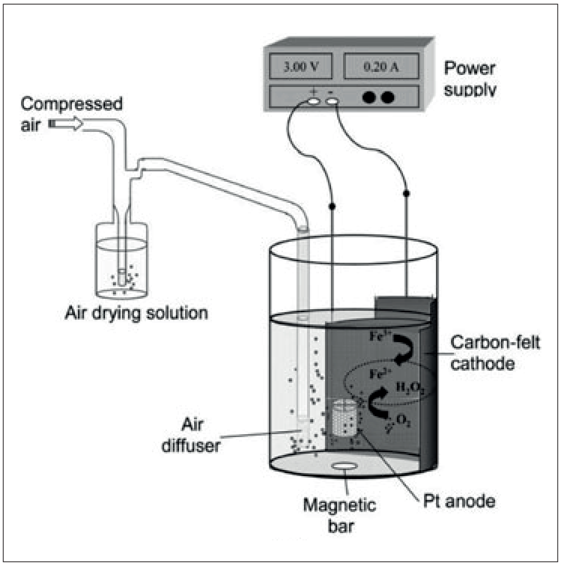

Fig. 2. The scheme of the electro-Fenton cell. Oxygen is introduced to the reactor via air bubbling. A magnetic bar is used to homogenize the solution while a power supply enables the electrochemical reactions on the cathode (production of H2O2 and Fe2+ ions) and anode surface. Ref. [15]

The main advantages of the electro-Fenton process are: in-site production of H_2O_2 from the air oxygen that avoid the risks linked to its transport, storage and handling, the use of low quantity of iron (II) ions that unable the formation of sludge, use of low cost electrodes. Electrochemistry is a very important technique from the environmental aspect because it uses only electrons for the production of hydroxyl radicals so electro-Fenton is considered a clean method for the overall oxidation of persistent organic pollutants.

Electro-Fenton process has been used in very efficient manner to remove from wastewaters plenty of persistent organic pollutants and toxic compounds such as synthetic dyes, pesticides, pharmaceuticals, personal care products etc. [20, 21] It was recently also applied to the soil remediation through the soil washing and flushing and the complete degradation of petroleum hydrocarbons and aromatic hydrocarbons. [22, 23]

The capacity of electro-Fenton process for a fast and complete removal of persistent organic pollutants can be increased by its coupling with a source of UV or visible light. The use of UV irradiation enables an additional quantity of hydroxyl radicals due to the H_2O_2 photolysis while some products of Fenton reaction, under the visible light are easily destroyed. The combination of solar energy with the electro-Fenton process is very important from the economical aspect because it can reduce the cost of electrical energy of lamps that furnish UV light. [24] Solar Photo Electro-Fenton tank reactors have been constructed for the complete mineralization of dyes and pharmaceuticals with an important diminution of energy consumption due to the use of photovoltaic energy as a cheap source of electrical energy. [25, 26]

During the complete degradation of some POPs it is necessary to spent high amount of electricity that may represent an obstacle for large scale treatment. In order to escape this inconvenience the electro-Fenton process which enables the transformation of recalcitrant and toxic molecules to biodegradable intermediates during a very short of the treatment and can be coupled with a biological treatment that enhances the total degradation of POPs from the water with a low cost procedure. [27, 28]

8. CONCLUSION

Advanced oxidation processes are very efficient techniques for the degradation of persistent organic pollutants. Their common point is the production of hydroxyl radicals by the activation of hydrogen peroxide in different ways: photochemically, chemically or electrochemically. These species are very reactive and transform, in a short period of time, the toxic organic molecules into carbon dioxide and water molecules. Electro-Fenton process also offers an alternative option for the production of hydroxyl radicals and is considered a cost effective and clean reagent. A combination of AOPs methods increases the rate of degradation of organic contaminants and the use of alternative energies can contribute to the diminution of the cost of water treatment process. Actually there are many attempts to pass from the academic research level of AOPs to real large-scale wastewater treatment plants.

REFERENCES

[1] Stockholm Convention on Persistent Organic Pollutants. *Official Journal of European Union*, L. 209/3. 31. 7. 2006.
[2] Regulation (EC) No 2018/0070 of the European Parliament and of the Council of 22 March 2018 on persistent organic pollutants recast.
[3] O. M. L. Alharbi, A, A, Basheer, R. A. Khattab, I. Ali. Health and environmental effects of persistent organic pollutants. *Journal of Molecular Liquids*, vol. 263, 2018, p. 442–453.
[4] M. A. Oturan and J. J. Aaron. Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. *Critical Reviews in Environmental Science and Technology*, vol. 44, 2014, p. 2577–2641.
[5] https://www.who.int/sustainable-development/cities/health-risks/water-sanitation/en/
[6] M. Lahti and A. Oikari. Microbial transformation of pharmaceuticals naproxen, bisoprolol, and diclofenac in aerobic and anaerobic environments. *Archives of Environmental Contamination and Toxicology*, vol. 61, 2011, p. 202–210.
[7] K. G. Pavithra, P. S. Kumar, V. Jaikumar, P. S. Rajan. Removal of colorants from waste water:A review on source sand treatment strategies. *Journal of Industrial and Engineering Chemistry*, vol. 75, 2019, p. 1–19.
[8] C. Grandclement, I. Seyssiecq, A. Piram, P. Wong-Wah-Chung, G. Vanot, N. Tiliacos, N. Roche and P. Doumenq. From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: A review. *Water Research*, vol. 111, 2017, p. 297–317.
[9] W. H. Glaze, J. W. Kwang and D. H. Chapin. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. *Ozone Science and Engineering*, vol. 9, 1987, p. 335–352.
[10] K. Turhan and S. Uzman. Removal of phenol from water using ozone. *Desalination*, vol. 229, 2008, p. 257–263.
[11] S. R. Sarathy, M. Mohseni. The impact of UV/H_2O_2 advanced oxidation on molecular size distribution of chromophoric natural organic matter. *Environmental Science and Technology*, Vol. 41, 2007, p. 8315–8320.
[12] H.-Y. Shu. Degradation of dye house effluent containing C. I. Direct Blue 199 by processes of ozonation, UV/H2O2 and insequence of ozonation with UV/H2O2. *Journal of Hazardous Materials*, vol. 133, 2006, p. 92–98.

[13] D. Spasiano, R. Marotta, S. Malato, P. Fernandez-Ibañez, I. Di Somma, Solar photocatalysis: materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach, *Applied Catalysis B Environment,* vol. 170–171, 2015, p. 90–123.
[14] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chemical Reviews*, vol. 95, 1995, p. 69–96.
[15] R. Hazime, C. Ferronato, L. Fine, A. Salvador, F. Jaber, and J. M. Chovelon. Photocatalytic degradation of imazalil in an aqueous suspension of TiO_2 and influence of alcohols on the degradation. *Applied Catalysis B Environmental*, vol. 126, 2012, p. 90–99.
[16] V. A, Sakkas, P. Calza, C. Medana, A. E. Villioti, C. Baiocchi, E. Pelizzetti and T. Albanis. Heterogeneous photocatalytic degradation of the pharmaceutical agent salbutamol in aqueous titanium dioxide suspensions. *Applied Catalysis B Environmental*, vol. 77, 2007, p. 135–144.
[17] E. Brillas, I. Sires and M. A. Oturan. Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. *Chemical Reviews*, vol. 109, 2009, p. 6570–6631.
[18] M. Panizza, P. A. Michaud, G. Cerisola, C. Comninellis. Anodic oxidation of 2-naphtholatboron-dopeddiamondelectrodes. *Journal of Electroanalytical Chemistry*, vol. 507, 2001, p. 206–214.
[19] F. Sopaj, N. Oturan, J. Pinson, F. Podvorica and M. A. Oturan. Effect of the anode materials on the efficiency of the electro-Fenton process for the mineralization of the antibiotic sulfamethazine. *Applied Catalysis B: Environmental*, vol. 199, 2016, p. 331–341.
[20] W. Yao, X. Wang, H. Yang, G. Yu, S. Deng, J. Huang, B. Wang and Y. Wang. Removal of pharmaceuticals from secondary effluents by an electro-peroxone process. *Water Research*, vol. 88, 2016, p. 826–835.
[21] M. A. Oturan, N. Oturan, M. C. Edelahi, F. I. Podvorica and K. El Kacemi. Oxidative degradation of herbicide diuron in aqueous medium bu Fenton's reagent based advanced oxidation processes. *Chemical Engineering Journal*, vol. 171, 2011, p. 127–135.
[22] D. Huguenot, E. Mousset, E. D. van Hullebusch, M. A. Oturan. Combination of surfactant enhanced soil washing and electro-Fenton process for the treatment of soils contaminated by petroleum hydrocarbons. *Journal of Environment Management*, vol. 153, 2015, p. 40–47.
[23] E. Mousset, N. Oturan, E. D. van Hullebusch, G. Guibaud, G. Esposito, M. A. Oturan. Influence of solubilizing agents (cyclodextrin or surfactant) on phenanthrene degradation by electro-Fenton process — Study of soil washing recycling possibilities and environmental impact *Water Research*, vol. 48, 2014, p. 306–316.
[24] C. Flox, J. A. Garrido, R. M. Rodriguez, P. L. Cabot, F. Centellas, C. Arias, E. Brillas, Mineralization of herbicide mecopropbyphotoelectro-Fenton with UVA and solar light Catalysis Today, vol. 129, 2007, p. 29–36.
[25] R. Salazar, S. Garcia-Segura, M. S. Ureta-Zañartu, E. Brillas. Degradation of disperse azo dyes from waters by solar photoelectro-Fenton. *Electrochimica Acta*, 2011, *56*, 6371–6379

[26] E. Isarain-Chávez, R. M. Rodríguez, P. L. Cabot, F. Centellas, C. Arias, J. A. Garrido, E. Brillas. Degradation of pharmaceutical beta-blockers by electrochemical advanced oxidation processes using a flowplant with a solar compound parabolic collector. *Water Research*, vol. 45, 2011, p. 4119–4130.
[27] H. Olvera-Vargas, T. Cocerva, N. Oturan, D. Buisson, M. A. Oturan, Bioelectro-Fenton:A sustainable integrated process for removal of organic pollutants from water: Application to mineralization of metoprolol. *Journal of Hazardous Materials*, vol. 319, 2016, p. 13–23.
[28] A. Arca-Ramos, E. Ammann, C. Gasser, P. Nastold, G. Eibes, G. Feijoo, J. Lema, M. Moreira, P.-X. Corvini. Assessing the use of nanoimmobilized laccases to remove micropollutants from wastewater. *Environment Science Pollution Research*, vol. 23, 2016, p. 3217–3228.