



Treball Final de Grau

Photoassisted processes for the removal of organic pollutants in aqueous medium.

Processos fotoassistits per a l'eliminació de contaminants orgànics en medi aquós.

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June 2018



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No hi ha vida sense aigua.

Albert Szent-Györgyi

First of all, I would like to thank my family, especially my grandmother, for trusting me and giving me the necessary strength throughout the degree. Without them, this would not have been possible.

I would also like to thank my mentor, Fermín Huarte, for all his energy at education and his great support during these years. At the same time, I would like to thank Ignacio Sirés, and also Roger, for making possible this project and for helping and teaching me everything they knew.

Last, but not least, I would love to name the person who made me know the wonderful world of chemistry and, thanks to her, today I am here wanting to learn more and more every day. She is my high school chemistry teacher, Anna Martí.

REPORT

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1. SUMMARY

The core of this project consists in a bibliographic study (sections 3 to 10). Lately, the study of the removal of organic pollutants from aqueous medium has become an issue of growing concern, due to their negative environmental impact as a result of the high toxicity of most of the xenobiotics released into wastewater.

Many organic compounds are very stable, resistant to common oxidants and non-biodegradable. Therefore, they cannot be eliminated by means of conventional water treatments. Some effective methods are: Fenton, photo-Fenton, photolysis or photoelectro-Fenton, among others.

The project has been completed with a small experimental work (sections 11 and 12), aiming to put into practice the concepts investigated in the bibliographic part. This work is focused on the degradation of a dye, namely Indigo Carmine, from water by different photoassisted processes.

Keywords: Dye, Indigo Carmine, Fenton process, organic pollutants, photoassisted process, photolysis.

2. RESUM

El treball consta principalment d'un recull bibliogràfic (de la secció 3 a la 10). L'eliminació de contaminants orgànics presents en el medi aquós és un tema que s'està estudiant molt en l'actualitat, a causa del seu l'impacte tan negatiu sobre el medi ambient com a resultat de l'elevada toxicitat de la majoria dels compostos sintètics avocats a les aigües residuals.

Molts dels compostos orgànics són estables, resistents front als oxidants comuns i no biodegradables. És per aquest motiu que no es poden eliminar mitjançant els tractaments d'aigua convencionals. Alguns mètodes efectius són: Fenton, foto-Fenton, fotòlisi o fotoelectro-Fenton, entre d'altres.

El projecte també inclou una petita part experimental (seccions 11 i 12), per tal de posar en pràctica els conceptes apresos durant l'estudi bibliogràfic. Aquesta secció es centra en la degradació d'un colorant, Carmí Indi, contingut en aigua mitjançant diferents processos fotoassistits.

Paraules clau: Carmí Indi, colorant, contaminants orgànics, fotòlisi, procés Fenton, processos fotoassistits.

3. INTRODUCTION

Water is essential for the subsistence of living beings, that is why it is so important. Water streams may contain three main classes of pollutants, namely inorganic or organic as well as microorganisms. Organic pollutants are especially relevant, since they are discharged into water bodies in large amounts, usually in released urban or industrial wastewater. Some of these pollutants are: industrial chemicals, pesticides, dyes and pharmaceuticals and personal care products. These pollutants have been produced by human activities (industrial, urban and agricultural). The majority of these compounds are considered as persistent organic pollutants (POPs), with high stability against sunlight irradiation and resistance to microbial attack and temperature. Hence, conventional wastewater treatment plants cannot remove these compounds. The pollutants are toxic and have potential hazardous health effects on living organisms [1]. Therefore, the development of simple, safe, effective and economical technologies for the total destruction of POPs is being intensely studied.

3.1. WATER POLLUTANTS

Some organic pollutants can be biodegraded by bacteria, but others are non-biodegradable. This work will address the technologies related to the treatment of this latter kind of pollutants. The following list includes some non-biodegradable organic compounds that are typically found in wastewater [1]:

- **Pesticides:** Toxic substances or mixture of substances created to prevent, destroy or repel pests. The problem of pesticides is that they can move from the application site into aqueous compartments, eventually polluting the aquifers and surface water. The organic pesticides contained in wastewater are biorefractory (they tend to remain in the environment indefinitely), and cannot be eliminated by conventional oxidation methods in municipal sewage treatment plants.

- **Dyestuffs:** The majority of these compounds are azo derivatives. Their presence in water can cause environmental problems, like eutrophication, under-oxygenation or color and odor change. Dyestuffs, like pesticides, cannot be destroyed by conventional treatments.

- **Pharmaceuticals:** The presence of pharmaceuticals and personal care products in water becomes an environmental problem as well. This is because pharmaceuticals have a potential toxicological effect on living organisms even at low concentration. Some of these compounds can alter the endocrine system of animals and contaminate the environment. Conventional sewage treatment plants are very inefficient to destroy pharmaceuticals. Additionally, they are resistant to degradation through biological or conventional chemical processes. Therefore, alternative methods using different chemical oxidants like Cl_2 , ClO_2 and O_3 are also investigated. The disadvantage of these oxidants is that they do not promote their total mineralization, unlike advanced oxidation processes [2].

- **Industrial pollutants:** Wastewater can contain industrial chemicals like phenol and phenolic compounds, anilines, benzene derivatives and aliphatic compounds, among others. Specific methods must be applied to remove them from water.

3.2. WASTEWATER TREATMENT PLANTS

The goal of wastewater treatment plants is to treat contaminated water and produce safe water for distinct applications. The sewage treatment is the process of removing contaminants from wastewater. It consists in physical, chemical and biological processes that are used to remove pollutants and produce treated water. The most typical sewage treatment involves four stages:

- **Pretreatment:** The aim of this process is to remove and separate large pollutants. It usually requires three steps; (i) roughing, which eliminates large pollutants, mainly insoluble solids, like rags, diapers, compresses and others; (ii) disbanding, for the elimination of sand or other non-organic solid waste of small size; and (iii) degreasing, to remove immiscible solids and liquids of lower density than water.

- **Primary treatment:** The main aim of this treatment is to separate the suspended particles in the water by physical processes. The most used physical process is decantation, but there are others: coagulation, flocculation or filtration.

- **Secondary treatment:** This treatment consists in biological processes to remove organic compounds by bacteria.

- **Tertiary treatment:** This treatment is based on a physicochemical conditioning. The objective of these processes is to remove the particles that the other treatments cannot do. For

this reason, these treatments are more specific for each pollutant and, consequently, more expensive. These processes are very important and necessary because they may ensure the disappearance of water pollutants. Consequently, the treated water can be used for many purposes like irrigation. This type of treatments will be studied in greater detail because they are the state of the art in the sector. Some of these treatments are: conventional oxidation processes, advanced oxidation processes (AOPs) and electrochemical advanced oxidation processes (EAOPs).

4. OBJECTIVES

The aim of this project is to make a thorough bibliographical survey about the removal of organic pollutants by photoassisted processes, in order to understand the reactions and mechanisms involved in each method.

In addition, the objective of the experimental section is to corroborate the different performance of the methods under study, finally obtaining some sound conclusion on the most effective treatment.

5. PRELIMINARY COMMENTS ON ELECTROCHEMICAL METHODS

5.1. ADVANTAGES

Some electrochemical methods can remove non-biodegradable compounds from wastewater with optimal efficiency. The importance of investigating in detail these methods in recent years is because POPs cannot be eliminated by conventional methods. That is why these methods are being developed, showing important advantages over conventional methods [3]:

- **Environmental compatibility:** The electrochemical methods can convert toxic compounds into products of low or null environmental impact. It is also considered a "clean" technology in the sense that it uses the electron as main reactant.

- **Versatility:** It is possible to use the same device to remove different toxic compounds without changes in the design or in the electrodes used.

- **Safety:** In electrochemical methods it is not necessary to store or use toxic reagents. Usually, needed reagents can be generated in the treatment site.

- **Selectivity:** Electrochemical methods have the possibility of controlling the potential of the working electrode. Consequently, it allows to control the desired electrochemical reaction.

- **Automation:** If the treatment is going to be used routinely for a determined type of waste, it is feasible to fully automatize the process.

- **Cost:** Although the type of installation implies an important economic investment and a considerable use of electric power, upon continued use of the system it is possible to pay off the investment. Moreover, the cost-effectiveness ratio is appropriate.

5.2. FIGURES OF MERIT

A figure of merit is a quantitative parameter used to characterize the performance of a device, system or method, compare to its alternatives. There are various figures of merit that are used as an indicator of the progress and efficiency of electro-oxidation of organic pollutants, but the most used in removal pollutants are current efficiency and specific energy consumption [3]:

- **Current efficiency:** It is the ratio of the charge used for the oxidation of each compound to the total charge passed during electrolysis. There are a lot of expressions to calculate the current efficiency. One of them is the instantaneous current efficiency (ICE), which is determined from the **chemical oxygen demand (COD)**. Another one is mineralization current efficiency (MCE), which is calculated from the **total organic carbon (TOC)**. The removal of organic pollutants will cause the decrease of COD and TOC.

- **Specific energy consumption:** It is the energy used to remove a unit mass of COD or TOC from wastewater. When the electricity cost is know, this parameter allows the calculation of the energy cost of the treatment.

5.3. INFLUENCE OF OPERATION PARAMETERS

The degradation rate of organic pollutants in water depends on operation parameters such as the anode material, solution pH, current density (j), temperature, solution composition, O₂ feeding, stirring rate or liquid flow rate, iron catalyst, initial pollutant concentration and the type of irradiation (solar/artificial) [4,5]. Generally, in all the methods, the influence is as follows:

- **Anode material:** The anode material is an important factor because it has a large influence on the efficiency of electro-oxidation process. There is a great assortment of electrodes: Pt, dimensionally stable anodes (DSA[®]) like DSA-Cl₂ and DSA-O₂, Ti/SnO₂, Ti/PbO₂ and boron-doped diamond (BDD), among the most relevant. Each electrode exhibits different oxidation power and each of them needs some experimental conditions recommended by the manufacturer. The best electrode is usually the one that yields a higher COD removal rate, which is the main aim during the removal of organic pollutants. Another factor that determines the selection is the price; for example, BDD is an expensive anode.

- **Solution pH:** This is an important parameter to preserve the effectiveness of some electrochemical oxidation processes. In Fenton-based processes, the maximum efficiency is found approximately at pH 3.0, since this leads to the maximum production of ·OH from Fenton's reaction [1].

- **Current density (j):** It is the electric current per unit area of cross section. If the current density is controlled, at an optimum value of j the electrochemical process will be controlled and it can: (i) avoid undesired parallel reactions, (ii) improve current efficiency and (iii) reduce energy costs. When the current density increases, a higher energy consumption is usually needed. The time needed to achieve the limit COD value rises when j decreases. Thus, a high value of current density is needed, but not the highest because it could cause the oxidation of other compounds (parasitic reactions). So, if parasitic reactions create undesirable compounds, the efficiency of the desired reaction will become lower, or it might even stop (Figure 1).

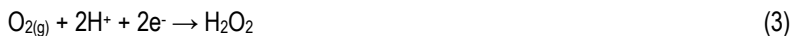
- **Temperature:** It usually has little influence in the COD removal rate. A temperature of 35-40 °C is appropriate because the mineralization rate increases. On the contrary, when temperature becomes greater, the mineralization rate decreases because of the strong acceleration of chemical H₂O₂ decomposition (reaction 1) in Fenton's reaction, as an example of process.



- **Solution composition:** In electrochemical water treatment there are two options regarding the electrolyte: (i) Wastewater or (ii) synthetic aqueous solution prepared to promote the production of oxidants and, after that, addition to the wastewater. Some salts, like NaCl or Na₂SO₄, are added as background electrolyte to increase the ionic conductivity. The concentration of Cl⁻ must be enough to form the necessary oxidizing species (hypochlorous acid may act as an oxidant). It has been studied that a higher concentration of Cl⁻ (reaction 2) is associated with a COD removal rate and lower energy consumption [2].



- **O₂ feeding:** Typically, high levels of O₂ (or air) are preferred, owing to two reasons: (i) To feed the gas-diffusion electrode (GDE) used as cathode, and (ii) to obtain the maximum H₂O₂ production rate (reaction 3). On the other hand, it is necessary that the GDE does not produce many bubbles because it increases the ohmic drop.



- **Stirring rate or liquid flow rate:** There are two ways to homogenize the solution and, in addition, enhance the efficiency of the reaction: (i) stirring, where the solution is magnetically or mechanically stirred to promote convection, and (ii) solution pumping, where the solution is circulated through tubes, in batch or continuous mode. In general, high stirring rate or liquid flow rate is preferred, thus favoring mass transport of reactants to and from the electrodes to yield the maximum rates of electrode reactions (Figure 2).

- **Iron catalyst:** In Fenton's reaction, the iron catalyst is Fe³⁺ or Fe²⁺. The maximum production of ·OH takes place at optimized Fe³⁺ or Fe²⁺ concentrations. However, at excessively high levels of catalyst concentration, inhibited reactions could appear (reaction 4) [1].



- **Initial pollutant concentration:** The initial pollutant concentration is important because it influences the degradation kinetics. An increase in initial pollutant concentration causes slower kinetics and lower values of COD removals.

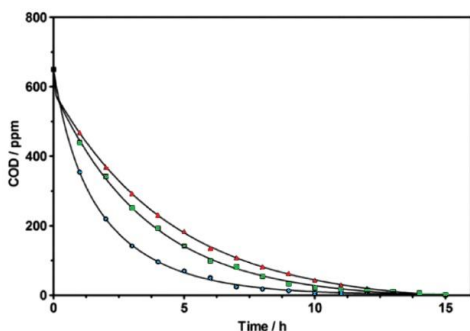


Figure 1. Effect of current density on the evolution of COD.

▲ 20 mA cm⁻², ■ 40 mA cm⁻², ● 60 mA cm⁻²

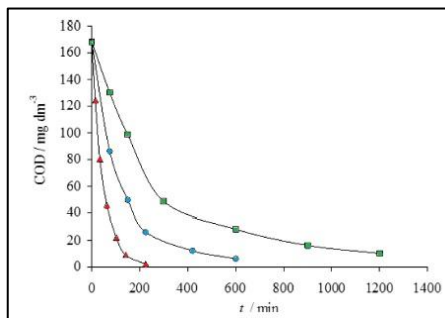


Figure 2. Effect of the electrolyte flow rate on the COD evolution.

▲ 180 dm³ h⁻¹, ● 100 dm³ h⁻¹, ■ 60 dm³ h⁻¹

(image extractea from Sirés, I. et al, ref. 4)

5.4. TYPE OF ELECTRODES

The anodes can be classified according to the efficiency of the oxidation process [2,3]:

- **Graphite, carbon-based electrodes with a metal (i.e., Pt, Ti/Pt), metal oxide electrodes (i.e., IrO₂, RuO₂) and mixed-metal oxide anodes:** These electrodes are low oxidation power anodes. So, they have low efficiency in the oxidation of organic pollutants (Figure 3), because they produce intermediates with small mineralization rates and sometimes polymers. These electrodes yield very low current efficiency and, for this reason, they are employed in fewer systems. Moreover, the carbon-based electrodes can be electrochemically incinerated (transformed to CO₂) when the method requires high voltages to oxidize the organic pollutants.

- **Other metal oxides, mixed-metal oxide electrodes (with PbO₂ and/or SnO₂) and conductive diamond electrodes (BDD):** They are high oxidation power anodes. Consequently, they have high efficiency in the oxidation of organic pollutants (Figure 3). The mineralization of the organic compounds is only limited by mass transport control, and the high efficiency arises from the low accumulation of intermediates.

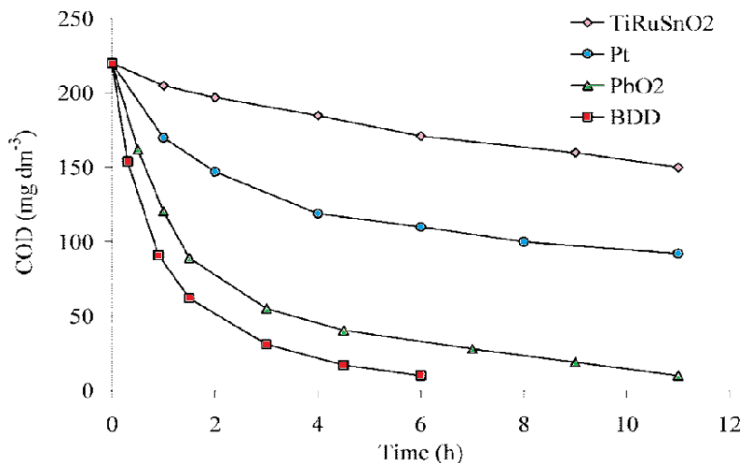


Figure 3. Comparison of COD during the electrochemical oxidation of Methyl Red at different anodes. The conditions are: $I = 500\text{mA}$ and flow rate = $180\text{ dm}^3\text{ h}^{-1}$.

(Image extracted from Panizza, M. et al, ref. 3)

6. PRELIMINARY COMMENTS ON ARTIFICIAL AND SOLAR LIGHT

An electrochemical process is a sequence of reactions that involve electric charges movement between electrodes and an electrolyte. These reactions are called redox (reduction/oxidation). A battery is an electrochemical system that provides energy. In contrast, if the reaction is not spontaneous, energy is required to promote it. Furthermore, an electrochemical process can be photoassisted with artificial light or solar light. Different types of light arise from the emission spectra according to the wavelength (Figure 4). Light may also be used to power the electrochemical devices.

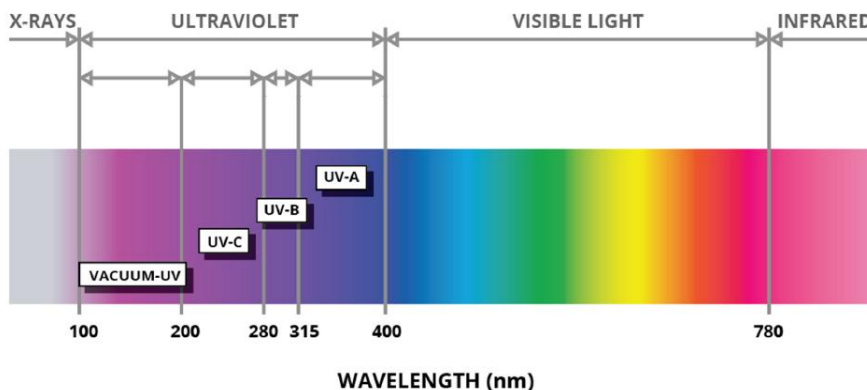


Figure 4. The UV region in the electromagnetic spectrum: UVA, UVB and UVC.
(Marktech Optoelectronics, 03/06/18)

Solar light is associated with photovoltaic cells (PVs), which are made of polycrystalline silicon [5]. Sunlight is free and renewable, so it is better to use this light if the conditions of the method are the appropriate ones. Solar light has many advantages: (i) the energy used is renewable, free, abundant and non-polluting, (ii) the use of PV energy decreases the investment cost of batteries and (iii) the long-life and low maintenance cost of the system [6].

The PVs can be connected in two ways: series or parallel. They can transform the solar radiation incident on the surface of PV into electric energy. In photovoltaics, batteries are frequently used. A battery consists of small accumulators that store energy through an electrochemical process. The purpose of a battery is to accumulate the energy produced by the photovoltaic panels during the hours of sun to be used in the dark or on cloudy days [6, 7].

On the other hand, there are different types of ultraviolet light: UVA, UVB and UVC. UV lamps are the devices that create ultraviolet light. The mechanism of UV lamps is explained thanks to the small amount of mercury which is in the lamps. When electricity is supplied to the lamp, the mercury is excited and emits UV light. The exact wavelengths emitted depend on the vacuum pressure within the lamp tube itself. For example, if there is a low pressure, UV will be UVC. Each method needs more or less powerful light to cause the reaction. A shorter wavelength gives more energy, a greater power of light. In conclusion, the power of light follows the sequence: UVC > UVB > UVA (Figure 4).

7. WATER TREATMENT BY PHOTOLYSIS

Photolysis is the breakdown of chemical bonds due to radiant energy. The result is the dissociation of molecules by the effect of light, and is defined as the interaction of one or more photons with a molecule. The type of light could be different (UVA, UVB or UVC) depending on the absorbance spectrum of the molecule. The most suitable type of light in photolysis is UVC since a powerful energy source is needed to break the bonds of the stable compounds. In photoassisted reactions, it is very important the photolysis of some compounds (H_2O_2 , O_3 , Cl_2) because they produce radicals (reaction 5, 6, 7), which are oxidative agents and hence, can mineralize organic pollutants. Note that reaction (6) does not produce radicals directly, but indirectly through reaction (5).



The photolysis of Cl_2 is less effective than that of H_2O_2 or O_3 , because chlorine radical ($E^\circ = 1.358\text{V}$ vs SHE) is less oxidative than hydroxyl radical ($E^\circ = 2.80\text{V}$ vs SHE).

8. WATER TREATMENT BY ADVANCED OXIDATION PROCESSES (AOPs)

Advanced oxidation processes (AOPs) are some type of processes designed to remove organic (and sometimes inorganic) non-degradable compounds from wastewater by different chemical oxidants (e.g., H_2O_2 , O_3 , Cl_2). This method is used in the tertiary treatment of a wastewater treatment plant. The aim of AOPs is to cause the abatement of the solution COD or TOC, as a consequence of the removal of organic compounds contained in the solution.

AOPs are characterized by the production of hydroxyl radicals ($\cdot\text{OH}$), which exhibit a high oxidizing power ($E^\circ = 2.80\text{V}$ vs SHE) and can easily break molecule bonds. This radical is very nonselective and rapidly reacts with numerous species with the rate constants in the order of $10^8 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [1].

AOPs are driven by external energy sources such as ultraviolet radiation (UV) or solar light. The speed of photochemical reactions with organic compounds can be increased by the addition to the medium of ozone, hydrogen peroxide or mixtures of both, because they are compounds that absorb ultraviolet light to produce radicals. As it was mentioned before, the photolysis of ozone and hydrogen peroxide originate hydroxyl radicals (reaction 5 and 6) [1].

The mechanism of AOPs involves several steps (Figure 5).

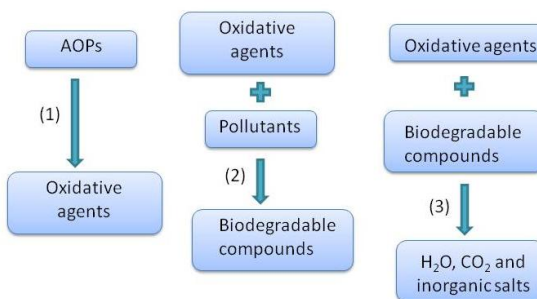


Figure 5. Steps of the mechanism of AOPs.

- (1) The production of strong oxidants ($\cdot\text{OH}$), which are the oxidative agents.
- (2) Oxidative agents react with the pollutants, which are organic compounds, and produce biodegradable intermediates.
- (3) The strong oxidants react with the biodegradable intermediates and they are mineralized, obtaining H_2O , CO_2 and inorganic salts.

Although AOPs have become a good technology for the removal of organic pollutants from all kinds of water matrices, they have a disadvantage: the high cost due to the use of expensive reagents. Consequently, AOPs are used only when the pollutants concentration is rather low ($< 5 \text{ g L}^{-1}$).

There are different methods to produce hydroxyl radicals in AOPs: $\text{H}_2\text{O}_2/\text{UV}$, O_3/UV , Cl_2/UV , photocatalysis, Fenton reaction, photo-Fenton and solar photo-Fenton (Figure 6).

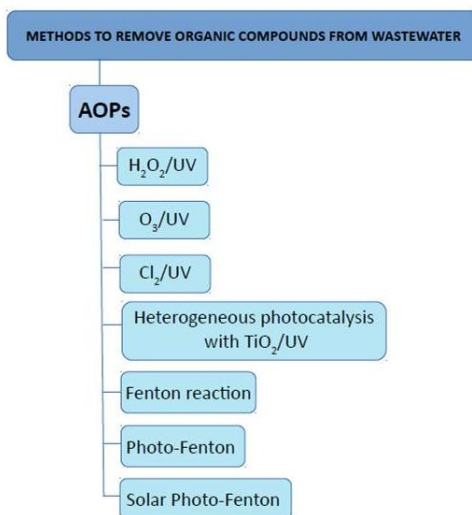


Figure 6. Scheme showing the types of AOPs.

8.1. H₂O₂/UV

Hydrogen peroxide is a strong oxidizing compound. Hydroxyl radical is produced via hydrogen peroxide, leaving oxygen gas and water (reaction 1 and 8).



This process with UV radiation (**H₂O₂/UV**), which is the AOP method, could be more efficient (reaction 5).

8.2. O₃/UV

Ozone is also a strong oxidant, although weaker than hydrogen peroxide. When it reacts with water (reaction 9), it may yield hydroxyl radicals.



If ozone is in presence of others oxidants or radiation, the $\cdot\text{OH}$ yield is increased. One example of AOP is the use of **O₃/H₂O₂** system (reaction 10). The details of the reaction are still not fully understood, so the research is in progress [8].



Another option is to irradiate the solution with ultraviolet irradiation (reaction 6), **O₃/UV**. This is a photochemical process where the compounds are irradiated. These compounds absorb the energy of the radiation to reach excited states where reactions take place.

8.3. Cl₂/UV

The oxidation of chloride ions produces Cl₂ (reaction 11). Therefore, water is reduced at cathode (reaction 12). At basic pH, Cl₂ is hydrolyzed and generates ClO⁻ (reaction 13). The hypochlorite ion has got high potential, so it can oxidize the organic compounds.



The potential of hypochlorite ion it is not as high as the hydroxyl radical. Therefore, it cannot oxidize all the organic compounds. For example, it is able to oxidize formaldehyde, phenol and glucose. Moreover, this method has got a disadvantage, which is the potential formation of volatile chlorinated compounds, and these compounds are more toxic and less biodegradable than the initial compounds.

Another option in this technology to become an AOP is to irradiate the solution with ultraviolet light, **Cl₂/UV**. The UV radiation enhances the efficiency of the process because of the production of Cl[•] (reaction 7).

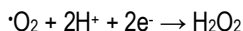
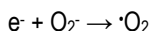
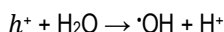
8.4. HETEROGENEOUS PHOTOCATALYSIS WITH TiO₂/UV

There are two types of photocatalysis: homogenous and heterogeneous. In this case, with TiO₂, it is a heterogeneous photocatalysis because the catalyst (TiO₂) is in a different phase from the reactants. A photocatalysis process is a method where the catalytic reaction involves the absorption of light by a catalyst or substrate, with the aim of accelerate a photoreaction using a catalyst. Even though there are many catalysts (Al₂O₃, ZnO, Fe₂O₃, TiO₂), the most used is Degussa P25 titanium dioxide (TiO₂) which is a semiconductor in the form of anatase 99% and rutile 1% [9]. It presents greater photocatalytic activity, it is not toxic, stable in aqueous solutions and not expensive. Different structures have been evaluated so far. With its absorption maximum approximately at 387 nm, TiO₂ absorbs in the near ultraviolet (UVA).

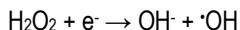
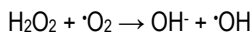
When the particles of TiO_2 are excited, the reaction produces positive charges (holes) in the valence band (h^+) that present an oxidative capacity and negative charges (electrons) at the conduction band (e^-) with a reductive capacity, as follows:



When OH^- , H_2O and O_2^- react with the particles formed at the surface of TiO_2 , free radicals (like $\cdot\text{OH}$) are generated, as shown in the sequence of reaction (15). Consequently, hydroxyl radical can remove the organic pollutants [1].



Both, the superoxide radical and the hydrogen peroxide generate more hydroxyl radicals (reaction 16). Later, these hydroxyl radicals can mineralize organic compounds.



The major loss of efficiency in this process arises from the recombination of electrons promoted to the valence band with either unreacted holes from reaction 17 or adsorbed $\cdot\text{OH}$ (reaction 18). So, both of them are parasitic reactions [1].



8.5. FENTON REACTION

There are some metals that activate H_2O_2 and produce hydroxyl radicals in water. In Fenton reaction (reaction 19), H_2O_2 reacts with iron, Fe^{2+} ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), to generate strong active species. In general, these oxidizing species are $\cdot\text{OH}$ [1].



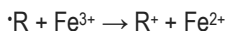
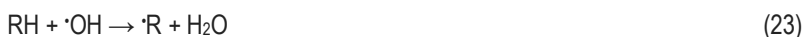
The Fe^{3+} formed can regenerate Fe^{2+} using the same hydrogen peroxide (so-called Fenton-like reaction). In addition, it another radical, HO_2^\cdot , is produced. It has a lower oxidation power than hydroxyl radical (reaction 20).



The previous reaction has got two steps (21, 22). In this process, it is important the formation of the adduct $[\text{Fe}^{\text{III}}(\text{HO}_2)]^{2+}$.



There is another option to regenerate iron, which is using organic radicals (reaction 23).



Fenton process presents important parasitic reactions, where H_2O_2 is destroyed. These reactions (reactions 20 and 24) compete with the Fenton's general reaction (reaction 19).



It is important to know that Fenton reaction has got one key condition to take place, which is the acidic pH. So, it has been demonstrated that the optimal pH to produce Fenton reaction is approximately 3. At this pH, the concentration of Fe^{2+} available in the solution is maximum in front of Fe(III) compounds. To conclude, Fenton reaction demands strict pH control of the treated solution. If the solution is too acid ($\text{pH} \ll 3$), reaction 19 would be inhibited. Conversely, if the solution has a $\text{pH} > 5$, the amount of total iron would decrease due to the precipitation of Fe(III) in form of $\text{Fe}(\text{OH})_3$ [1].

Fenton reaction is very efficient because it produces hydroxyl radicals without an external energy supply. In contrast, it has got a disadvantage. Its performance is limited when the solution contains dissolved anions such as phosphates, chlorides or nitrates. These anions can form complexes with iron and, consequently, decrease the capacity of iron to react with H_2O_2 . So, the reaction ends. This problem can easily avoided by removing the anions before Fenton process, with separation methods [10].

The reaction finishes when all the H_2O_2 has reacted.

8.6. PHOTO-FENTON

The photo-Fenton process has got the same mechanism as Fenton process, but the key difference is that solution is irradiated with UVA with the purpose of enhancing the efficiency of the reaction and induce the reduction of Fe(III) to Fe²⁺. This process is generally used when the objective is reducing COD at high levels.

Hydroxyl radicals are formed in the same way as in Fenton reaction, where the large accumulation of Fe(III) species decelerates the treatment. This drawback is avoided with the reductive photolysis of [Fe(OH)]²⁺ (reaction 25) [1, 11].



In addition, UV radiation can induce the photodegradation of some oxidation byproducts or their complexes with Fe(III), as for example carboxylate species (reaction 26). They promote Fe²⁺ regeneration as well [1].



The advantages of this method are that it is an efficient treatment to remove organic pollutants from wastewater with a high efficiency and at low operation cost.

8.7. SOLAR PHOTO-FENTON

This method is the same as photo-Fenton process but, instead of using artificial light (UVA), sunlight is used as energy source [1]. The mechanism is the same, but the use of sunlight presents many advantages, which are mentioned in section 6. The two most important advantages are: the cost of the process, because it eliminates the price of UVA lamps, and the renewable nature of sunlight [6].

9. WATER TREATMENT BY ELECTROCHEMICAL METHODS

There are different types of electrochemical methods. The main characteristic is the relevant role of electrochemistry. Electrochemical methods include electrochemical advanced oxidation

processes (EAOPs) and electrocoagulation. Their design is similar but electrocoagulation is not considered an EAOP. This is because electrocoagulation is a non-degradative technique, but it rather promotes the separation of compounds by means of an electrogenerated coagulant. In contrast, EAOPs allow degradation, since oxidizing agents are electrosynthesized, thus leading to the mineralization of the organic matter.

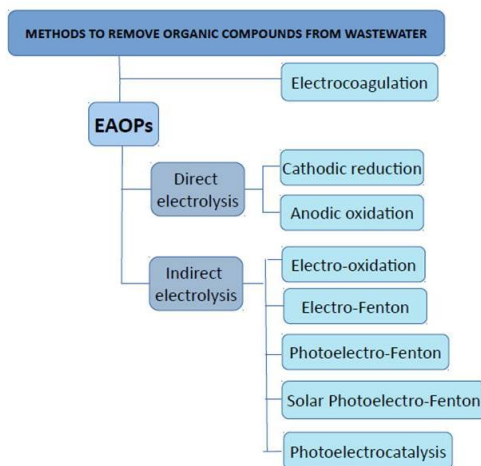


Figure 7. Scheme showing the electrochemical methods.

9.1. ELECTROCOAGULATION

Electrocoagulation is a suitable technique to remove suspended solids and particles able to flocculate, like some pollutants in wastewater. This method it is not appropriate when soluble organic matter is the main pollutant to be removed [5].

The organic compounds that are in the aqueous medium can appear in different forms: suspended, emulsified or dissolved. In electrocoagulation process, these compounds are destabilized by an induced electric current between the anode and the cathode (Figure 8). The most used anodes are aluminum and iron. The coagulant is formed in situ by the reactions given by the dissolution of metal anode. So, anode is the electrode which provides metal ions, being called sacrificial anode [6, 12].

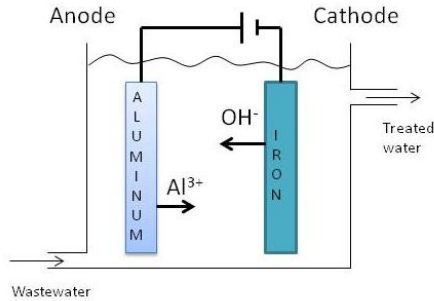


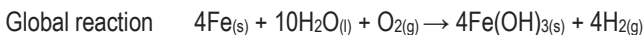
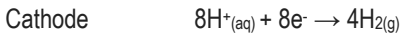
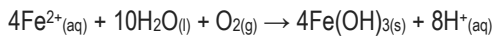
Figure 8. Schematic diagram of electrocoagulation, where aluminum acts as anode and iron as cathode.

The electric current in this process is essential because it provides the electromotive force that causes a series of chemical reactions, whose final result is the destabilization of the polluting molecules. The process produces solid particles less emulsified or soluble than the initial ones. When it occurs, the pollutants form hydrophobic components that precipitate and, because of that, its removal is facilitated by some secondary separation method.

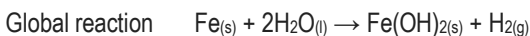
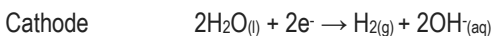
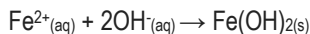
The metal ions are released and dispersed in the medium. They form metallic oxides that electrically attract the pollutants that have been destabilized.

In the case in which iron acts as the anode, two possible coagulants may be formed: Fe(OH)_2 and Fe(OH)_3 . The formation mechanism of Fe(OH)_3 (reaction 27) and Fe(OH)_2 (reaction 28) are the following [12, 13]:

- Formation of Fe(OH)_3

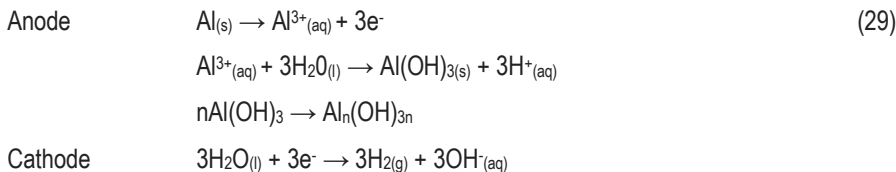


- Formation of Fe(OH)_2



Another option is the case when aluminum acts as the anode, where the coagulant formed is $\text{Al}(\text{OH})_3$ (reaction 29) [12, 14].

- Formation of $\text{Al}(\text{OH})_3$



$\text{Al}_n(\text{OH})_{3n}$ is produced because Al^{3+} and OH^- can react to form various monomeric species. Finally, by precipitation processes, $\text{Al}(\text{OH})_3$ is formed.

Some applications of the electrocoagulation process are the sewage treatment, where, for example, the electrocoagulation followed by an electroflotation process has been used to remove chromium from wastewater. If electrocoagulation process is not able to reduce COD under discharge limits that are established by regulations, an additional treatment must be used before the wastewater is discharged. Another important application is the destabilization and removal of emulsions (oil-water), oils and fats that have been generated by the mechanical industry, the refineries, the automotive repair shops, the transport and distribution and storage of oils [12, 14].

Even though this method is suitable to remove different types of pollutants, it also shows some disadvantages: (i) continuous dissolution of sacrificial electrodes, (ii) cost of electricity, (iii) formation of an oxide at the anode, thus the passage of electric current and reducing the efficiency of process, and (iv) the need of high conductivity. However, there are some advantages: (i) it needs a simple equipment, (ii) operation and easy automation, (iii) fast sedimentation rates and (iv) high effectiveness in the removal of a wide range of contaminants [14].

9.2. ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (EAOPs)

For a while and at present, more efficient methods to remove toxic and non-biodegradable pollutants from wastewater with a high efficiency are being developed. These methods are called electrochemical advanced oxidation processes (EAOPs). They are similar to AOPs but

the role played by electrochemistry is crucial. So, chemical reactions are triggered by an externally applied potential difference. These processes are clean and effective techniques.

There are two general types of electrochemical methods: direct and indirect electrolysis [3, 15].

9.2.1. Direct electrolysis

The pollutants are electrolyzed at the electrode. This process can occur by two means; (i) direct electronic transfer (reduction or oxidation) to or from the organic compound, or (ii) chemical reaction of the pollutant with previously electrogenerated species that remain adsorbed on the electrode surface. A direct electrolysis includes cathodic reduction and anodic oxidation.

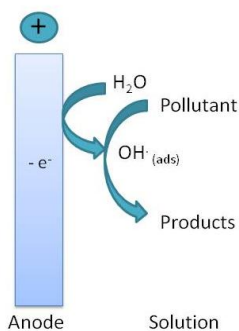


Figure 9. Process of direct electrolysis

In Figure 9, the pollutant, which is an organic compound, reacts with adsorbed hydroxyl radicals. Hydroxyl radicals are produced from the oxidation of water on the anode at high oxygen overpotential. This process is called “direct electrolysis by anodic oxidation”, because the reaction takes place at the anode and the radicals are produced by the oxidation of water.

9.2.1.1. Cathodic reduction

As it has been mentioned previously, cathodic reduction is included in direct electrolysis. In this process, a reduction of the pollutant occurs at cathode. One condition is that this technique is carried out only when the pollutants are in wastewater at low concentrations. The most used application of this method is the dehalogenation of organic chlorinated compounds. The most used chloro-organics are: solvents (CHCl_3 , CCl_4), freezer compounds (CFCs), pesticides and others. The general reaction to remove each atom of chlorine is given by reaction 30 [15].



This reaction competes with the evolution of H_2 . Therefore, cathodes with a high overpotential of H_2 evolution are employed to get the highest efficiency in the reaction. The products of this reaction are less toxic and more biodegradable than the reactive but the efficiency of the reaction is low.

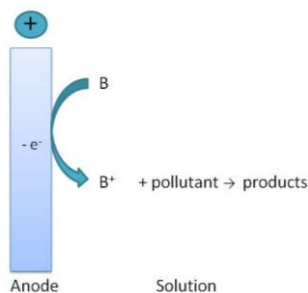
9.2.1.2. Anodic oxidation

The anodic oxidation is a frequently used method, based on direct electrolysis. It can remove organic compounds like anilines and phenols, among other. The reactions in this method with an inert anode are very slow and hence, electrocatalytic anodes (Pt, IrO₂, RuO₂, PbO₂, SnO₂) are employed at high anodic potentials. As it has been mentioned before, under these conditions, hydroxyl radicals are produced and adsorbed on the anode (reaction 8).

The radical characteristics make the hydroxyl radical an optimum weapon against organic compounds, because radicals are unstable. Consequently, they have a very short half-life and they are very reactive. Specifically, the hydroxyl radical is the second most oxidizing species known ($E^\circ = 2.80$ V vs SHE), after fluorine. So, this radical can react quickly with the pollutants and transform them in their hydroxylated or dehydrogenated derivatives, and finally, mineralize them. Mineralization of an organic compound means its complete oxidation to yield CO₂, inorganic ions and water [1].

9.2.2. Indirect electrolysis

In this type of electrolysis, the pollutant is removed in solution by different active species which are produced at the electrode. Some of these active species, which are strong oxidants, are: O₃, ClO⁻, Cl₂ and ClO₂. In addition, there are some others methods included in indirect electrolytic methods: (i) Phase separation methods, like: electrocoagulation, electroflocculation and electroflotation and (ii) EAOPs [3, 15].



In Figure 10, the pollutant reacts in solution with a species (B⁺) generated by the oxidation of an inactive species (B) at the anode.

Figure 10. Process of indirect electrolysis

Regarding the possible removal of pollutants, there are two different ways to do it [15]:

- **Electrochemical transformation:** The non-biodegradable compounds are transformed in biodegradable ones, which then remain stable in solution.

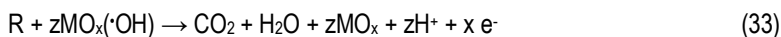
- **Electrochemical combustion:** All the pollutants are completely mineralized.

It has been studied that there are some electrodes that stimulate an electrochemical transformation, whereas others promote the electrochemical combustion. The reason of this is explained by Comninellis and co-workers, who supposed that the surface of the anode is formed by an oxide (MO_x) [15]. Hydroxyl radicals can then be adsorbed on the anode (reaction 31) or they can transfer oxygen to the MO_x and formed the super metal oxide MO_{x+1} (reaction 32).



In these reactions (31 and 32), it can be seen that there is active oxygen of two kinds: physisorbed ($\cdot OH$) and chemisorbed (MO_{x+1}) on the anode.

When this active oxygen is physisorbed in presence of an organic compound (R) that is in solution, a complete electrochemical combustion occurs (reaction 33). On the other hand, when active oxygen is chemisorbed, an electrochemical transformation takes places, where RO are the partially oxidized products (reaction 34).



The stoichiometry of the reaction 33 depends of the pollutant, and “z” accounts for that in order to show a general reaction.

In anodic oxidation, both kinds of reaction (33, 34) can occur, but one is predominant over the other. This depends on the oxygen evolution overpotential and the deterioration of organic compounds.

In addition, Comninellis has studied the anodes that favor an electrochemical transformation and an electrochemical combustion [15], which can be observed in Table 1.

ELECTROCHEMICAL TRANSFORMATION	ELECTROCHEMICAL COMBUSTION
Pt	Doped SnO ₂
IrO ₂	Doped and undoped PbO ₂
RuO ₂	BDD

Table 1. Corniellis classification of anodes depending on the electrochemical process.

In the electrochemical combustion process, two types of reaction can occur: hydroxylation (reaction 35) or dehydrogenation (reaction 36) of organic compounds (R or R'H).



From reaction 36, the organic radical R'· could react with oxygen. This yields a hydroperoxyl radical (R'OO·) (reaction 37). This radical is active enough to uptake a hydrogen atom from another pollutant (R''H) (reaction 38).



The hydroperoxyl generated in reaction 38 is unstable and can be mineralized to finally produce CO₂, inorganic ions and water.

In conclusion, an electrochemical process can appear as a transformation or combustion electrochemical process.

As it has been said above, EAOPs can occur through a direct or indirect electrolysis. The EAOPs that are generally based in indirect electrolysis are: electro-oxidation, electro-Fenton, UV photoelectro-Fenton, solar photoelectro-Fenton and photoelectrocatalysis.

9.2.2.1. Electro-oxidation

This method can be an indirect or direct electrolysis, such as it is mentioned in previous sections. An EO process involves an oxidation reaction that is promoted by an external potential.

9.2.2.2. *Electro-Fenton*

The mechanism of this method involves the degradation of organic compounds with hydroxyl radicals produced in solution by a reaction between the catalyst Fe^{2+} and the electrogenerated H_2O_2 in the electrolytic cell. In summary, EAOPs are based on the fundamentals of AOPs (Fenton process), with the difference that in EF the H_2O_2 is electrogenerated in situ. An oxygen-diffusion cathode is used to electrogenerate the H_2O_2 by reducing the oxygen (reaction 3). At the same time, Fe(III) may be cathodically reduced to regenerate Fe^{2+} (reaction 39). If the anode is a material with a large oxygen evolution overpotential, it favors the simultaneous $\cdot\text{OH}$ production from the oxidation of water (reaction 8) [1, 2].



9.2.2.3. *Photoelectro-Fenton*

As it was mentioned before, the PEF is the same process as EF, but the solution is irradiated with UVA light. The radiation enhances the efficiency because: (i) The stable form of Fe(III) is $[\text{Fe(OH)}]^{2+}$; the radiation causes the reduction of the stable form in hydroxyl radicals and regenerates Fe^{2+} (reaction 25), and (ii) this radiation allows the mineralization of stable complexes that are formed between Fe(III) and short chain carboxylic acids. These complexes are generated in the last stages of the contaminant mineralization process (reaction 26).

9.2.2.4. *Solar photoelectro-Fenton*

The mechanism of this method is the same as in PEF but with one difference: the radiation sources is the sun. So, the energy source is clean and renewable. The radiation characteristics mentioned in the previous section are also applied in this method.

Consequently, and in general, a faster TOC removal is in the sequence: $\text{EF} < \text{PEF} < \text{SPEF}$ (Figure 11). EF is a good method to remove organic pollutants but PEF is better because of the presence of UV irradiation. Finally, most of the times, SPEF is the best process because of its greater irradiation intensity entering into the solution [1].

9.2.2.5. *Photoelectrocatalysis*

It is a powerful photoelectrochemical treatment derived from the combination of heterogeneous photocatalysis and electrochemical techniques. The mechanism of the process is the same as in photocatalysis.

It is important to know that when a high photocurrent increases the oxidant production, the degradation rate of pollutants is limited by diffusion transport because the pollutants must diffuse to the catalyst surface. Although this method is very effective, there are some disadvantages: (i) additional oxidant species produced on the catalyst surface can be consumed by parasitic reactions; this would entail a decrease in the mineralization and degradation efficiency of pollutants, and (ii) the low applied j (limited by the low stability and conductivity of the anode surface at high potentials) causes a partial mineralization.

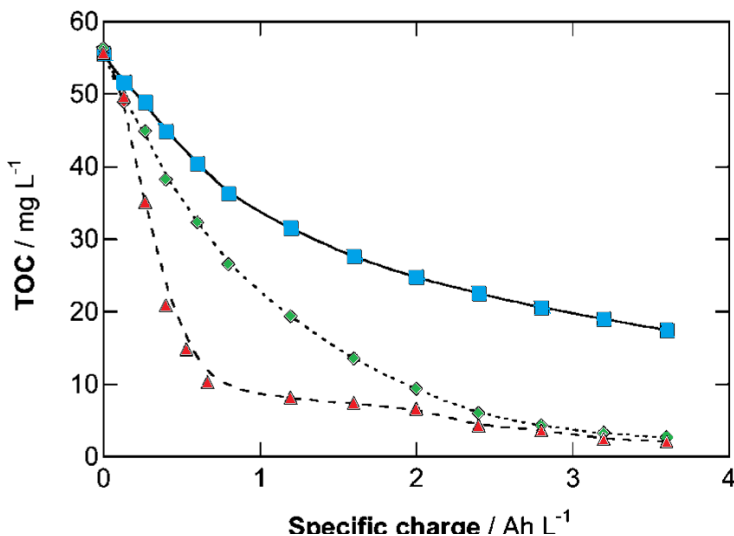


Figure 11. TOC removal with specific charge for different methods: Electro-Fenton (EF), Photoelectro-Fenton (PEF) and Solar photoelectro-Fenton (SPEF).
(Image extracted from Brillas, E. et al, ref. 1)

10. APPLICATIONS

TrojanUV is a current company in Spain, with leadership in the development of technological equipment for the treatment of water using ultraviolet light. Currently, TrojanUV has the largest number of references on the planet of UV systems installed in operation. This company has a wide range of machines depending on the type of pollutant (pesticide, pharmaceutical) and the medium conditions (the flow of water and others). Some machinery for the treatment of pollutants in water are: TrojanUVSwift™ECT and TrojanUVPhox™ [16].



Figure 12. Machinery for the treatment of pollutants.
TrojanUVSwift™ECT (left) and TrojanUVPhox™ (right).

(Trojan Technologies, 18/04/18)

One example of a TrojanUV application is in the groundwater under San Gabriel Valley (California). It was determined that in groundwater there were volatile organic compounds (VOC), in particular trichloroethylene, perchloroethylene and 1,4-dioxane.

1,4-Dioxane cannot be removed by conventional methods and hence, ultraviolet light was used to cause its oxidation. The hydroxyl radicals produced by UV oxidation effectively destroy 1,4-dioxane.

The machinery to perform this treatment was TrojanUVPhox. The result was a removal of approximately 98% of 1,4-dioxane, treating 2.5 MGD of groundwater polluted. The aim to do this was to supply drinking water for 1.000.000 people in California. In conclusion, the TrojanUV application is really effective [16].

11. EXPERIMENTAL ASSAYS

Some of the methods explained previously have been put into practice in this project, with the aim of verifying the theory studied. All the experiments have been done with Indigo Carmine (IC) as model pollutant, which is an important dye used for coloring textiles, specifically blue jeans. In this section, the materials and methods employed are described.

11.1. CHEMICALS

The reagents used to prepare each initial solution are:

- IC (Aldrich, 85% of purity): It is the main reagent. IC is an organic salt derived from Indigo (I) by sulfonation. It is used as dark blue powder [17-18].

Chemical formula	Chemical name	Color index name	Other names	λ_{\max} (nm)	<i>M</i> (g/mol)
$C_{16}H_8O_8N_2S_2Na_2$	3,3'-dioxo-2,2'-bisindolyden-5,5'-disulfonic acid disodium salt	Indigo Carmine	Indigotine Brilliant Indigo E132	611	466.36

Table 2. Characteristics of Indigo Carmine

IC has got a chromophore group in its structure (Figure 13), which is responsible for the UV absorption. As it is known, the complementary color of reagents is the responsible of the color. So, in this case, the complementary color of blue is orange. Orange absorbs at wavelengths between 581 and 618 nm. Therefore, this is why Indigo Carmine absorbs at 611 nm and it is blue [17].

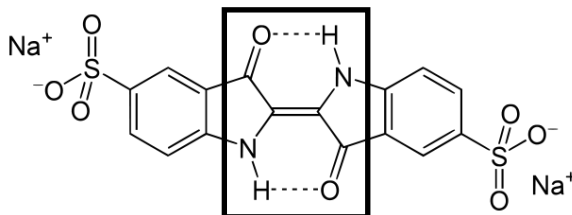


Figure 13. Chemical structure and the chromophore group of IC.

- Anhydrous sodium sulfate (Na_2SO_4 , VWR, 98.5% of purity): It is used as a background electrolyte.

- Concentrated sulfuric acid (H_2SO_4 , Panreac, 95-98% of purity): IC is not very soluble in water due to the strong intermolecular forces caused by hydrogen bonds. Instead, it is soluble in acid medium ($\text{pH} = 3$).

11.2. FIXED EXPERIMENTAL CONDITIONS

Concentration of reagents in the initial solution	Temperature [°C]	Treated volume [mL]	Duration of the process [min]	Sampling time [min]	Measurements
50 mg/L TOC of IC mixed with 50 mM Na_2SO_4 at $\text{pH} = 3$ (adjusted with H_2SO_4)	25	150	180	30	TOC ($t = 0$ and $t = 180$ min) Absorbance at each sampling time

Table 3. Experimental conditions kept constant in all the experiments.

11.3. SPECIFIC EXPERIMENTAL CONDITIONS

Six experiments have been done in order to eliminate IC from the aqueous solutions:

	F	H ₂ O ₂ photolysis	Cl ₂ photolysis	PF	PEF	PEC
[H ₂ O ₂] [mM]	10	10	-	10	-	-
[Fe ²⁺] [mM]	0.5	-	-	0.5	0.5	-
[Cl ₂] [mM]	-	-	10	-	-	-
Lamp	-	UVC, 8 W	UVC, 8 W	UVA, 36 W	UVA, 36 W	UVA, 36 W
Electrodes	-	-	-	-	Air-diffusion cathode BDD anode	Air-diffusion cathode TiO ₂ nanotubes anode
Electrode area [cm ²]	-	-	-	-	3	3
Current density [j, mA/cm ²]	-	-	-	-	33.3	3

Table 4. Specific experimental conditions in each trial: Fenton (F), H₂O₂ photolysis, Cl₂ photolysis, Photo-Fenton (PF), Photoelectro-Fenton (PEF) and Photoelectrocatalysis (PEC). FeSO₄·7H₂O was used as the source of Fe²⁺, and commercial NaClO (40 g/L Cl₂) was employed as active chlorine source.

11.4. EQUIPMENTS AND ANALYTICAL PROCEDURES

The decolorization of IC solutions was monitored by the decrease of their absorbance at the maximum visible wavelength of 611 nm. It was recorded on a Shimadzu 1800 UV-vis spectrophotometer. Aliquots were always diluted (2 mL of sample, 3 mL of water) to ensure that Lambert-Beer's Law was accomplished. The spectra of the solutions were monitored between 200 and 800 nm.

The mineralization of IC solutions was assessed from their TOC abatement. In this study, TOC is equivalent to TC because solutions were at acidic pH, thus preventing the accumulation of inorganic carbon. Organic compounds contained in the IC solutions are converted into CO₂ inside the combustion chamber 600-700 °C of a Shimadzu TOC-V analyzer. TOC values were

obtained injecting 50 μL aliquots into the analyzer. All samples were diluted, when needed, to be below 30 mg/L.

12. RESULTS AND DISCUSSION

12.1. COLOR REMOVAL

In order to assess the decrease in absorbance at the maximum wavelength (611 nm) of IC, the spectrum of the initial solution that only contains IC has been recorded (Figure 14). The other peaks, within the UV region, belong to other parts of the dye structure, as well as to some impurity. For example, *o*-nitrobenzaldehyde, which is the main reagent to form synthetic IC ($\lambda_{\text{max}} = 290\text{nm}$) [19-20].

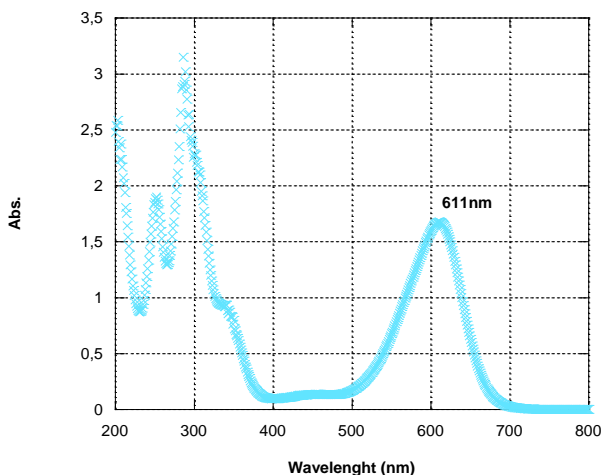


Figure 14. Indigo Carmine spectrum showing its $\lambda_{\text{max}} = 611\text{ nm}$.

Along the experiments, the solution is decolorized, in agreement with the expected IC removal upon main action of the hydroxyl radicals created in each process (Reactions 5, 6, 9, 10, 15, 16, 19, 25), as well as active chlorine and chlorine radicals (Reaction 2, 7, 11, 13) in the case of Cl_2 photolysis. All these species act as strong oxidants that cause the cleavage of the

chromophore group, yielding either colored or colorless intermediates. Depending on the effectiveness of the process, the solution will be decolorized at different speed. The initial solution is blue, but when IC is disappearing, it goes through colors like orange and yellow until a practically colorless solution is obtained (Figure 15). The different nature and proportion of the intermediates accounts for the varied coloring observed during the degradation processes. Some intermediates are anthranilic acid (2-aminobenzoic acid), which provides a yellowish color and has got the maximum retention time of the intermediates, and Isatin, which can be responsible for an orange color [20].



Figure 15. Solution color at different reaction times during the degradation of IC by F, as an example. The trend is similar for all treatments.

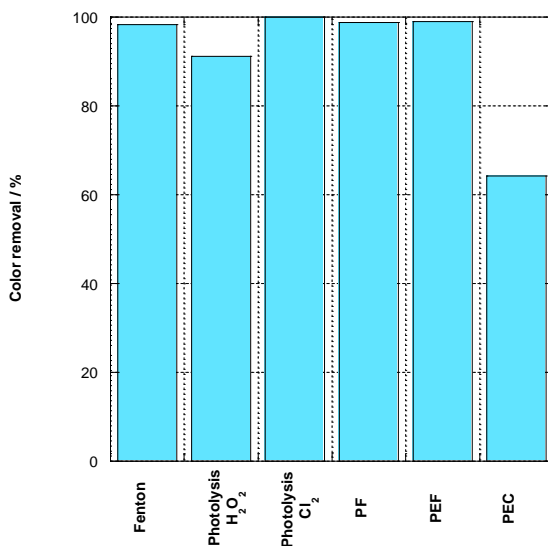


Figure 16. Percentage of color removal at $\lambda_{max} = 611$ nm after 30 min for the degradation of 150 mL of 50 mg/L IC solution by different processes: Fenton, Photolysis H_2O_2 , Photolysis Cl_2 , Photo-Fenton (PF), Photoelectro-Fenton (PEF) and Photoelectrocatalysis (PEC). At pH = 3 and T = 25 °C

In Figure 16, it can be observed that the decolorization is almost complete at 30 min in all treatments, except in PEC. Therefore, the absorbance study indicates that the reactive species generated (chemically, electrochemically or photochemically) in each process are very powerful to break the chromophore structure of IC and its reaction by-products. In the case of PEC, however, the low applied j (limited by the low stability and conductivity of the anode surface at high potentials) ended in a partial color removal after 30 min.

12.2. TOC REMOVAL

TOC measurement is the best indicator of IC mineralization during the process. The aim of the applied AOPs and EAOPs is not only to remove IC, but also its reaction intermediates, which can be even more toxic.

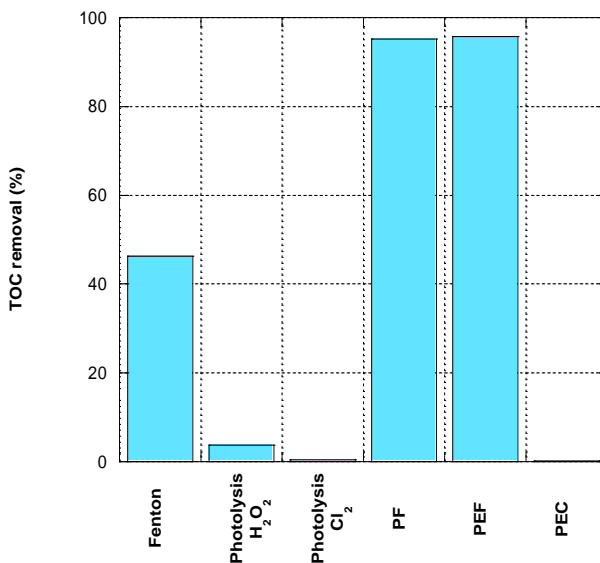


Figure 17. Percentage of TOC removal at final time ($t = 180$ min) by different processes: Fenton, Photolysis H_2O_2 , Photolysis Cl_2 , Photo-Fenton (PF), Photoelectro-Fenton (PEF) and Photoelectrocatalysis (PEC).

The experimental results (Figure 17) observed in TOC study indicate that the efficiency of PF and PEF processes is much greater than the others because it greatly reduces TOC

solution. In contrast, Photolysis and PEC processes practically do not decrease TOC. Fenton-based technologies are thus the most suitable ones to treat dyes in water at acid pH.

13. CONCLUSIONS

Taking into account absorbance and TOC studies, it can be concluded that the oxidation power on IC solutions increases in the sequence: PEC < Photolysis Cl₂ < Photolysis H₂O₂ < Fenton < PF ~ PEF.

The main conclusions extracted from the project about this sequence are the following:

- PEC presents the lowest oxidation power due to the low j , which is limited by the low stability and conductivity of the anode surface at high potentials.

- Photolysis processes are quite inefficient in organic pollutants removal because they produce low amounts of radicals. H₂O₂ photolysis is more efficient than Cl₂ photolysis. That is because hydroxyl radicals are more oxidizing than chlorine radicals.

Therefore, chlorine radicals only break weaker bonds of organic compounds, which is why there are uncolored intermediates with stronger bonds, which can only break the hydroxyl radicals.

- Fenton process has a higher efficiency due to the large amount of hydroxyl radicals that are produced. The disadvantage of this process is the formation of stable intermediates, which makes the process not as efficient as it could be.

- In PF and PEF, the stable intermediates can be photolyzed thanks to UVA radiation, and this explains the high efficiency and the almost total mineralization.

14. REFERENCES AND NOTES

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15. ACRONYMS

AOPs	Advanced oxidation processes
BDD	Boron-doped diamond
COD	Chemical oxygen demand
EAOPs	Electrochemical advanced oxidation processes
EF	Electro-Fenton
EO	Electro-oxidation
F	Fenton
IC	Indigo Carmine
ICE	Instantaneous current efficiency
MCE	Mineralization current efficiency
PEC	Photoelectrocatalysis
PEF	Photoelectro-Fenton
PF	Photo-Fenton
POPs	Persistent organic pollutants
PVs	Photovoltaic cells
SPEF	Solar Photoelectro-Fenton
TOC	Total organic carbon

