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Utilización de especies de hierro complejadas para procesos fotoquímicos de tratamiento de aguas

Trabajo Fin de Máster

Máster Universitario en Ingeniería, Procesado y Caracterización de Materiales

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SUMMARY

" Use of complexed iron species for photochemical processes of water treatment "

Hydrogen peroxide is decomposed into various species, by means of the photo-Fenton reaction, among them being hydroxyl radicals (·OH), which are highly reactive. This is due to the ability of iron salts to catalyse the decomposition of H_2O_2. However, an increase in the pH of the medium can lead to the formation of inactive iron compounds or their precipitation.

To mitigate this formation and keep the iron active, there are various organic species or materials that are capable of complexing it. One type of these materials is organic matter, in particular humic acids (HA), which will be studied in the present work. To this end, the effect of organic matter on the photo-Fenton process will be observed, acting both homogeneously and heterogeneously, with the use of nanoparticles with a magnetite centre and coated with humic acid.

In the same way that there are compounds that improve the process, there are also others that cause specific problems and drawbacks. Among these compounds are different inorganic salts, such as chlorides or phosphates. In the present work, the effect of these two types of ions on the medium is observed, as well as whether the HA can mitigate their impact.

RESUMEN

" Utilización de especies de hierro complejadas para procesos fotoquímicos de tratamiento de aguas "

Mediante el proceso foto-Fenton, el peróxido de hidrógeno es descompuesto en diversas especies, entre ellas los radicales hidroxilo (·OH), los cuales presentan una elevada reactividad. Esto ocurre gracias a la capacidad de las sales de hierro para catalizar la descomposición del H_2O_2. No obstante, un aumento del pH en el medio puede producir la formación de compuestos de hierro inactivos o su precipitación.

Para mitigar esta formación y mantener el hierro activo existen diversas especies o materiales de carácter orgánico que son capaces de complejarlo. Un tipo de estos materiales es la materia orgánica, en particular los ácidos húmicos (HA), que serán estudiados en el presente trabajo. Para ello, se observará el efecto de la materia orgánica en el proceso foto-Fenton actuando tanto de manera homogénea como de manera heterogénea, con el uso de nanopartículas con el centro de magnetita y recubiertas con ácido húmico.

Por otra parte, así como hay compuestos que mejoran el proceso, también hay otros que causan problemas e inconvenientes en el proceso. Entre estos compuestos se encuentran diferentes sales inorgánicas, como los cloruros o los fosfatos. En el presente trabajo se observa el efecto de estos dos tipos de iones sobre el medio, así como si los HA pueden mitigar su impacto.

Palabras clave: Fenton; hierro; contaminantes; catalizadores; radiación UV-visible

RESUM

" Utilització d'espècies de ferro complexades per a processos fotoquímics de tractament d'aigües "

Mitjançant el procés foto-Fenton, el peròxid d'hidrogen és descompost en diverses espècies, entre elles es radicals hidroxil (·OH), els quals presenten una elevada reactivitat. Això ocorre gràcies a la capacitat de les sals de ferro per a catalitzar la descomposició del H_2O_2. No obstant això, un augment del pH en el mig pot produir la formació de compostos de ferro inactius o la seua precipitació.

Per a mitigar aquesta formació i mantindre el ferro actiu existeixen diverses espècies o materials de caràcter orgànic que són capaços de complexar-lo. Un tipus d'aquests materials és la matèria orgànica, en particular els àcids húmics (HA), que seran estudiats en el present treball. Per a això, s'observarà l'efecte de la matèria orgànica en el procés foto-Fenton actuant tant de manera homogènia com de manera heterogènia, amb l'ús de nanopartícules amb el centre de magnetita i recobertes amb àcid húmic.

D'altra banda, així com hi ha compostos que milloren el procés, també hi ha uns altres que causen problemes i inconvenients en el procés. Entre aquests compostos es troben diferents sals inorgàniques, com els clorurs o els fosfats. En el present treball s'observarà l'efecte d'aquests dos tipus d'ions sobre el mig, així com si els HA poden mitigar el seu impacte.

Paraules clau: Fenton; ferro; contaminants; catalitzadors; radiació UV-visible

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ABBREVIATIONS

AOPs	Advanced Oxidation Processes
ACP	Acetamiprid
AMOX	Amoxicillin
ASW	Artificial sweeteners
AZMF	Acetaminophen
BPA	Bisphenol-A
CAF	Caffeine
CAT	Catechol
CBZ	Carbamazepine
CEC	Contaminants of Emerging Concern
CLOF	Clofibric acid
DBP	Disinfection by-products
DW	Distilled Water
EDCS	Endocrine-disrupting compounds
EDDS	Ethylenediamine-N,N'-succinic acid
EPR	Electron Paramagnetic resonance
FR	Flame retardants
HA	Humic acids
HPLC	High-performance liquid chromatography
HSW	High salinity water
LSW	Low salinity water
PBDE	Polybrominated diphenyl ethers
PhAc	Pharmaceuticals and personal care products
PPCP	Pharmaceuticals and personal care products
TOC	Total organic carbon
TrOC	Degrading trace organic pollutants
WWTP	Wastewater treatment plants

FIGURE LIST

TABLE LIST

1. INTRODUCTION

1.1 Background

Water is an essential resource, decisive for the development of the human being and civilisation since it is necessary for agricultural irrigation, industrial uses or its consumption.

Although this resource is the most abundant that can be found on the earth's crust, 97% is seawater, which is not competent for consumption or agricultural uses. Regarding the 3% corresponding to freshwater, 75% is in the form of ice or snow. [1] The other 25% is still sufficient for human consumption worldwide; the problem is that this is not distributed equally everywhere, as seen in Figure 1.

Up to date, desalination technologies are still extremely expensive; therefore, further research on this topic, as well as technology related to wastewater reclamation, is required to approach water scarcity. Therefore, a viable option is using water from wastewater treatment plants (WWTPs) for further use in agriculture, industry or livestock farming. However, this type of water also presents a problem after its treatment: the presence of Contaminants of Emerging Concern (CECs) and microorganisms. In view of the new European regulations, these CECs (which include antibiotics, pesticides, etc.) must be treated and eliminated from the effluent. For this purpose, there are a series of processes called Advanced Oxidation Processes (AOPs), which are capable of degrading the CECs and disinfecting the water, also avoiding the formation of carcinogenic compounds such as trihalomethanes, which appear due to the use of chlorination. [2]
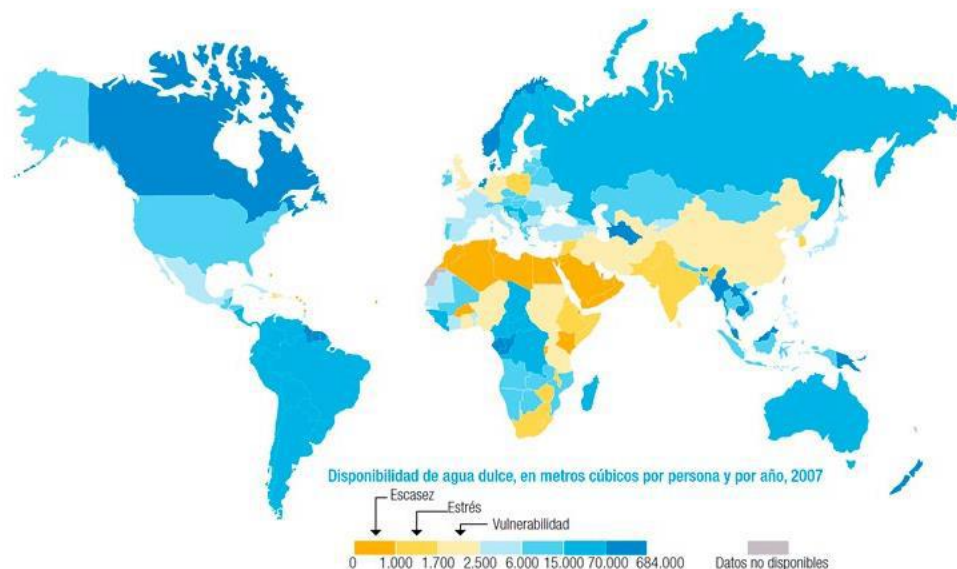
Figure 1. Availability of fresh water on the Earth in 2007.

1.2 Water contaminants

Since ancient times, waste derived from human activity has been accumulated in rivers, lakes and seas. The water cycle is a natural process with a great purification capacity; however, this elimination cycle can not eliminate specific contaminants discharged into the water.

According to the IUPAC definition, a pollutant is "any undesirable matter, solid, liquid or gaseous present in the environment; the quality of "undesirable" is determined by its concentration." Therefore, following the same organism, pollution is the "introduction of pollutants into the environment or any modification of the environment." [3]

The pollution produced in the waters can come from two origins, natural (e.g. arsenic in water) and anthropogenic (e.g. pesticides in water). Sources of natural origin are found in places scattered around the Earth. On the other hand, sources of pollution of human origin are usually located in specific areas and the concentration of pollutants discharged presents high values; therefore, they offer a greater danger. For the

latter, the classes of pollutants (and generated by-products due to partial degradation within a natural environment) discharged into the environment are significantly higher.[4]

To differentiate the pollutants present in the waters, a wide variety of classifications can be used, depending on their chemical, biological, physical characteristics... For example, an interesting classification is based on the toxicity of these in the environment, which would serve as a basis for selecting the treatment to be used in each case. This refers to those compounds with an ecotoxic and bioaccumulative character, which have a special regulation in the legislation of discharges, which are based on lists of products very harmful to the environment, the so-called 'black and grey lists. The substances found in these lists cannot be discharged into the environment above the stipulated concentration values or ensures their elimination through a series of treatment processes.[5]

List I of Polluting Substances (Black List) (Directive 76/464/CEE; R.D. 849/86)

1. Organohalogen compounds and substances which may give rise to organohalogen compounds in the aquatic environment.

2. Organophosphorus compounds.

3. Organotin compounds.

4. Substances which possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment.

5. Mercury and mercury compounds.

6. Cadmium and cadmium compounds.

7. Mineral oils and hydrocarbons of petroleum origin (both persistent and non-persistent).

8. Persistent synthetic substances which may float, remain in suspension or sink and thereby cause harm to any water use.

9. Cyanides.

List II of polluting substances (grey list)

1. The following metalloids and metals and their compounds: zinc, copper, nickel, chromium, lead, selenium, arsenic, antimony, molybdenum, titanium, tin, barium, beryllium, boron, uranium, vanadium, cobalt, thallium, tellurium, silver.

2. Biocidal products and their derivatives not listed in Schedule I.

3. Substances which have an adverse effect on the taste and/or odour of products for human consumption derived from the aquatic environment, as well as compounds liable to cause such effects in water.

4. Toxic or persistent organosilicon compounds and substances that may give rise to them in water, excluding those that are biologically harmless or rapidly transformed into harmless substances.

5. Inorganic phosphorus compounds and elemental phosphorus.

6. Fluorides.

7. Substances which adversely affect the oxygen balance, in particular the following: ammonia and nitrites.

1.3 Conventional water treatments

Before water discharge from rainwater and urban uses into the natural environment, it is treated in WWTPs. In these plants, three steps are followed for its purification being, firstly, a pre-treatment separating solids such as wet wipes, branches or sand. Subsequently, the primary treatment is carried out, where compounds with a higher density than water precipitate, while those with a lower density float. A settling tank is used for this purpose. Finally, the secondary treatment is carried out, based on the use of activated sludge biological reactors to degrade the biodegradable urban wastewaters.

However, to be able to use WWTP water safely for irrigation or industrial use, a minimum of water quality is needed from a chemical point of view. Therefore, it would be correct to apply an additional treatment at the end of the WWTP process, which is tertiary treatment. For this purpose, AOPs are presented as one of the most viable processes for implementation. [2]

With that, the increase in the number of wastewater loads, the increasingly restrictive laws of effluent discharges and the growing ecological awareness that looms over the planet, lead to the study of new methods of decontamination which can carry out the elimination and treatment of unwanted reagents present in the water. This is because these are usually harmful either to the health of people, fauna or flora of the environment.

For the treatment of this type of water, a series of processes can be used that vary depending on the way of acting on the contaminant. Below, a summary outline of each type of process with its primary examples will be shown.[6]

1.3.1   Physical treatments

Physical methods are not destructive and transfer these contaminants to other media, which must be treated later to remove the reagent from the new medium to which it has been transferred. This second process makes its use more expensive and complicated.

The main examples of this type of treatment would be sedimentation, in which separation occurs due to the effect of the gravity of those contaminants in the solid state that have a density greater than that of the liquid; flotation, where solid pollutants are less dense than liquid are collected at the surface; filtration, which ensures that contaminants, including solids, are trapped inside or on the surface of a medium with porosity; evaporation, producing vaporisation of either a liquid or a suspension of the solution; adsorption, which fixes the contaminant to a solid, removing it from the solution; desorption-stripping, eliminating the contaminant because it passes from the liquid solution to the air that comes into contact with it; and finally the extraction, in which the pollutant of the solution is transferred to a liquid not miscible with it.[6]

1.3.2   Biological treatments

They can be classified into two groups, depending on whether they need the presence of oxygen, aerobes, or their absence, anaerobes.

In the case of aerobes, different processes can be observed, such as bacterial filters, where the liquid flows through support that contains microorganisms; active sludge, in which the microorganisms are in suspension with the contaminated liquid mass; aerated lagoons, a process similar to the previous one but where large surface and low depth ponds are used; and biodisks, which are based on a mixed process between filters and sludge, since the support of microorganisms is partly submerged. [6]

1.3.3   Thermal treatments

A series of processes called thermal is also used, which are based on the decomposition of pollutants through high temperatures. In this case, the organic compounds are broken down into CO_2, water and halogen gases. The two major drawbacks of these processes are, on the one hand, the large amount of energy needed and, therefore, its cost. On the other hand, the appearance of unwanted intermediates.

In this treatment, three main types are concentrated. These are: i) wet oxidation, employing air between 150 and 325ºC is used at pressures between 2000 and 20000 KPa, which is put in contact with the liquid to eliminate very toxic contaminants that are at low concentrations; ii) supercritical oxidation, which is carried

out at a temperature and critical pressure 374ºC and 25'3 MPa; iii) incineration, where through combustion, pollutants are thermally destroyed.[6]

1.3.4   Chemical treatments

Contaminants are chemically oxidised or converted into other products. Then, these new products are more biodegradable.

Redox processes are a suitable method for reducing certain contaminants present in wastewater. Through this treatment, the oxidation state or number of the reacting species changes as an exchange of electrons between them occurs. For this, it is necessary the presence of a species that gives up electrons (reducer) and another species that accepts them (oxidant). In this way we find two processes in the reaction: oxidation, a process in which electrons are generated; that is, there is a loss of electrons by the reactant that is oxidised; and reduction, in which the electrons ceded by the other reactant are obtained. [6]

Two examples of this type of process are chlorination and ozonation. Although they are capable of being effective against CECs elimination, the principal disadvantage of these techniques is that they are expensive, due to the infrastructure and the energy needed, and sometimes they produce some carcinogenic compounds known as disinfection by-products (DBP). [2]

1.4 Contaminants of emerging concern (CECs)

Contaminants of emerging concern refer to a series of substances recently found in natural water worldwide in concentrations of ng - µg/L, with still unknown toxicological or environmental risks. These types of pollutants can be divided into several groups, including pharmaceuticals and personal care products (PPCPs), endocrine-disrupting compounds (EDCs), flame retardants (FRs), pesticides, artificial sweeteners and their metabolites (ASWs), and many other daily consumed substances.[7]

One of the significant problems with these types of pollutants is that they cannot be removed or treated by conventional wastewater treatment processes. This can be easily observed when analysing WWTP effluent, where several CECs are frequently detected in the effluent. Thus, WWTPs are one of the main sources of CECs released into the environment, since once the water is treated, it is released into the environment. However, the non-treatment of these pollutants can cause them to enter rivers and seas, affecting aqueous ecosystems as well as people if this type of water is consumed. This contributes to the contamination of river water, groundwater and, in several cases, drinking water. This phenomenon has been observed in different areas around the world, such as France, Ethiopia, Brazil, Southern California, South China, and Turkey.

Although several technologies have been used for the removal of CECs, such as reverse osmosis or the use of activated carbon, they have not been able to degrade them completely. Therefore, the use of advanced oxidation processes (AOPs) has been implemented as an alternative treatment for removing CECs. This is due to the fact that this type of technique is one of the most practical when it comes to achieving biodegradation and detoxification of WWTP discharges into the environment.[7] The importance of achieving the complete elimination of CECs is based on the fact that it is widely known that they have a negative impact on aquatic ecosystems, as well as on human health.

1.4.1   Pharmaceuticals and personal care products (PhACs)

PhACs have a high relation to lethal causes in case of overdose by their decontrolled consumption.[8] Organic substances (natural or synthetic) usually produce pharmaceuticals, and they are used to cure and prevent disease in patients as well as to enhance both human and animal quality of life.[9] Analgesics antimicrobials or antiepileptic medicines are among the numerous chemical compounds found in PPCPs.[10] PPCPs may remain intact after they are treated through WWTPs or have been transformed into another PPCP. Their presence in WWTPs is, in part, because they are not always completely digested by the body and can be expelled as an unmodified or active metabolite of the parent chemical.

One of the biggest hazards to societies, according to the World Health Organization, is antibiotic-resistant microorganisms.[11] For example, bacteria resistant to tetracycline and sulphonamides were present in the effluent from WWTPs in Michigan, USA.[12] With that, significant sources of antibiotics discharged into the environment have their principal source in urban WWTPs and hospital wastewater.[13]

Additionally, a variety of uses for personal care products may be found in daily life as antimicrobial agents to eliminate microorganisms.[14] The most important problem with personal care products is their lipophilic nature because they can threaten the ecosystem since they can be bioaccumulated.[15]

1.4.2   Endocrine-disrupting compounds

It is known that endocrine disruptors are absorbed by the body and create health problems by interfering with normal bodily processes, in addition to mimicking or blocking hormones. EDCs are substances including phenols, phthalates, and bisphenol-A (BPA) that may disrupt hormone or endocrine functions.[16] In addition, BPA exposure during human life may cause serious harm to the reproductive system, prenatal or antenatal development (low birth weight babies), metabolic disease (heart disease, hypertension, type 2 diabetes and cholesterol), among other health-related effects as a disruption of thyroid hormones.[17]

1.4.3   Flame retardants

Halogenated flame retardant compounds, such as polybrominated diphenyl ethers (PBDEs), and phosphorus-containing flame retardant compounds, such as organophosphate ester flame retardants, are two of the most common FR families. Carpets, laptops, polyurethane foams, electronic cables, and other components are made primarily using PBDEs as FRs.[18] Moreover, WWTPs sludge can be a significant source of FRs (such as organophosphate ester flame retardants) released into surface water; as a result, aquatic habitats get contaminated. The primary property of PBDEs is hydrophilia, which makes it easier for them to absorb into WWTP sludge.[19]

1.4.4   Pesticides

Pesticides, including aniline derivatives, organochlorides or organophosphates, have grown to be a major problem in modern times. There is evidence that certain pesticides play a significant role in disrupting hormones by affecting the glucocorticoid hormone receptor, a crucial component of the endocrine system. As a result, they may have several negative health consequences.[20] Due to the inability of urban WWTPs to completely remove pesticides, the discharge from these facilities is a significant contributor to the presence of pesticides in the aquatic environment.[21]

1.4.5   Artificial sweeteners

ASWs, a family of CECs that includes sucralose, acesulfame or saccharin, are often employed in high amounts as sugar replacements in foods, beverages, medicines, and sanitary items.[22] ASWs are typically eliminated through urine since they are not often digested (most stay unaltered). These intact sweeteners (like acesulfame) or sweeteners that have only partially undergone metabolism (like saccharin and sucralose) end up in the environment. The biggest problem with ASWs is that WWTPs can not degrade them all, such as acesulfame or sucralose.[23]

1.5 Treatments against CECs: Advanced oxidation processes (AOPs)

As mentioned above, CECs have very low or no treatment in WWTPs as conventional water treatment methods fail to remove them. This is why it is necessary to look for alternative treatments to remove them from the water before it is discharged again. There are different methods that can be used to study the degradation of CECs, such as the use of reverse osmosis membranes and activated carbon. However, these are separative methods, and they do not remove the pollutants. Therefore, AOPs are a great field of study because they are able to disinfect, degrade CECs, and avoid the formation of carcinogenic compounds like DBPs.[2]

These types of techniques are among the most practical when it comes to achieving biodegradation and detoxification of WWTP discharges to the environment. However, they have high treatment costs due to the use of UV lamps, which are very expensive.[24] To reduce this effect, several efforts are being made to perform these techniques with the use of solar radiation or the addition of catalysts in order to achieve effective and cheap treatments that can be implemented in the industry. Thus, most studies focus on the development of photo-Fenton, solar photo-Fenton and heterogeneous photocatalysis-based technologies.[25]

However, there is a problem with toxicity in different compounds. In many cases, the intermediates that appear due to the degradation of the original CECs have higher toxicities than these, which is also a major challenge to overcome.[26]

AOPs are technologies that use potent radical oxidants (such as $\cdot OH$ and SO_4^{-}) to produce the elimination of recalcitrant organic pollutants. With a typical reduction potential of 2'8 V vs standard hydrogen electrode, $\cdot OH$ is one of the most highly reactive radical species found in AOPs. This is due to the reaction between CEC and $\cdot OH$ being benefited thermodynamically (E0 = 2'80) and kinetically. For this, it is known that these radicals are non-selective, removing all the organic matter present in the mix.[27]

Among the techniques that involve AOPs, it can be found those based on:

- Ozonation (e.g. O_3/UV)

- Sonochemical processes

- Heterogeneous photocatalysis (e.g. TiO_2/UV)

- Fenton reaction

1.5.1   Ozonation

The ozonation technique may significantly enhance the effluent quality of WWTPs by degrading trace organic pollutants (TrOCs), offering safe drinking water available. Depending on the conditions under which ozonation is carried out, there are two types of ozonation: direct (basic media) or indirect (acidic media). [28] Zhao et al. 2016, carried out research on the use of ozone to remove the common pesticide thiamethoxam. This study showed that ozone molecules selectively react with it in three different ways: electrophilic reactions, which are based on ozone reactions with electron-donating groups with specific functional groups (e.g., -CH_3), nucleophilic reactions, based on ozone reactions with electron-leaving groups (-Cl) and dipole addition reactions, which are based on ozone reactions with double chain bonds (e.g., C=C and C=N).[29]

An interesting effect on the increase of oxidation rates was shown in different studies thanks to the combination of ozone with other techniques (such as UV or photo-Fenton).[30] The use of different ozone-based AOPs for removing four selected parabens in different water matrices, among them ultrapure water or WWTP effluent using $\cdot OH$, was examined.[31]

They claimed that compared to previous ozone-based AOPs, the O_3/UV/TiO_2/H_2O_2 combination was more efficient at eliminating parabens. Numerous studies have shown that the primary downsides of the process include labour-intensive treatment, high operating cost due to the energy and the equipment needed, a drawn-out procedure, poor TOC removal and the development of TPs (by-products) which, sometimes, are more toxic than the original products. [32]

Numerous investigations showed the presence of antiviral medications in surface, WWTPs and drinking water. These investigations concentrated on the elimination of these antiviral compounds. Schlüter-Vorberg and colleagues studied using ozonation techniques to remove acyclovir (an antiviral compound). During the nitrification process, acyclovir was converted into carboxy-acyclovir, and after ozonation, N-(4-carbamoyl-2-imino-5-oxoimidazolidin) formamide-n-methoxy-acid was produced. With that, it is shown how by trying to remove one compound, more toxic products can appear. [33]

1.5.2   Sonochemical processes

There has been a lot of interest in creating AOP-based ultrasonic procedures to degrade CECs. For instance, it was explained how sound waves with frequencies between 20 and 1000 kHz might penetrate a liquid and cause acoustic cavitation.[34] With this technique, bubbles are formed, grown, and then adiabatically collapsed to raise the temperature to 5000k and pressure to 200 atm. The decomposition of the H_2O into $\cdot OH$ and $\cdot H$ should be enough to start the pyrolytic process due to high temperatures. To explain how ultrasounds can stimulate the elimination of organic pollutants, two hypotheses are proposed: Pyrolysis, a heat degradation process, and interaction with $\cdot OH$.[35]

Recent research has demonstrated that using ultrasound together with Fenton, persulfate ions, or H_2O_2 results in the efficient elimination of CECs.[36]

1.5.3   Heterogeneous photocatalysis

Heterogeneous photocatalysts using semiconductors, such as TiO_2 nanoparticles, to eliminate CECs from water matrices have been highly studied recently. Due to its properties of being cheap, nontoxic, and resistant to photo corrosion, TiO_2 is regarded as a potential photocatalyst semiconductor for the removal of organic pollutants.[37] The use of TiO_2 in combination with solar photocatalytic wastewater treatment has been the focus of several researchers' work up until now.[38]

Full-scale use of TiO_2 nanoparticles was researched for the treatment of water, being one of their advantages its possible use at neutral pH values. In this study, solar energy in conjunction with TiO_2 and H_2O_2 system was performed, along with the difficulties and solutions for doing so. They claimed that mass sedimentation of nano-TiO_2, which made separation difficult, was one of the main downsides of its use.[39]

Because of its large band gap of 3'2 eV, TiO_2 only can absorb less than 5% of the solar spectrum (UV radiation with a wavelength lower than 387 nm). In recent years, to improve the photocatalytic oxidation properties of TiO_2, numerous studies have been performed to increase its light activity. These efforts include surface modification and ion doping (metal and non-metal).[40]

Because of the idea of electron capture, which makes surface-charge separation easier, researchers have concentrated on the idea of doping TiO_2 with different metal ions as a new modification strategy. As a result, the TiO_2-metal enhances the life of the charge carrier and increases the absorption of visible radiation.[41]

1.5.4   Fenton reaction

One of the most promising of the AOPs for water treatment is the Fenton-based process. This process is based on the capacity of iron ions to catalyse hydrogen peroxide decomposition, producing hydroxyl radicals ($\cdot OH$) in some of the elemental steps of this reaction.[42] These radicals are highly reactive, attacking all organic compounds present in the medium, such as, in this case, the CECs.

The process is based on the Haber-Weiss reaction, in which the two most elemental reactions are:

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \cdot + H^+ \qquad (2)$$
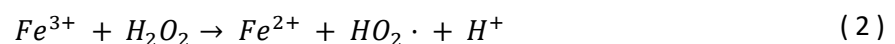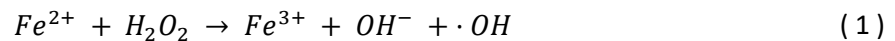
This reaction, which can occur naturally in aquatic ecosystems, can be applied in aquatic engineering systems to achieve water purification.

One of the most critical and slowest points of the Fenton-type processes is the regeneration of iron(II) (2). For this purpose, it has been studied that, through the application of UV-visible light, this process is greatly improved thanks to the decomposition of one of Fe(III) complex, following the following reaction:

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + \cdot OH \qquad (3)$$

This process is known as photo-Fenton, where the application of sunlight or UV lamps improves the main Fenton process. For its study, solar simulators or pilot plants can be used, and they can later be applied to the treatment of natural water.

Although this system is very convenient, there is a problem that makes it difficult to apply it to water treatment, which is the deactivation of iron. This occurs because, among other causes, $Fe(OH)_2^+$ presents a maximum at pH 2'8. At pH > 3'5, iron begins to precipitate, losing efficiency. Therefore, an important field of research on the process is to get the iron to remain active at pH values close to 7'0. Within this field, a recent avenue of research is based on the formation of photoactive compounds formed by Fe(III) and different organic ligands, such as ethylenediamine-N,N'-succinic acid (EDDS), oxalate, citrate... Since these must be added to the medium, one of the key factors is their biodegradability, as well as their potent toxicity. [2]

On the other hand, in the same way that there are certain compounds that allow an improvement of the Fenton-type processes, there are also many compounds that interact and stop or worsen the speed of the degradation process. Thus, the effects of chlorides, carbonates or phosphates have been studied and are well known.[43]

1.5.4.1 Iron ligands: humic acids

The presence of iron in aquatic media plays a very important role for living organisms, as it is used and necessary for their growth. However, its solubility at pH values where these organisms develop is very low, thus limiting its availability.[44] Thus, most of the iron present in aquatic systems is found in complex form through organic Fe-binding ligands.[45] For that, these ligands can present an important role in iron complexing to enhance the Fenton processes at pH above 3'0.

These ligands can have different origins, such as being generated from the transformation of natural organic matter or being produced by different microorganisms. Therefore, an interesting source of iron ligands would be the siderophore production by microorganisms.[46]

These siderophores are iron chelates that serve to capture iron in micro-organisms, which is why bacterial cells produce them. They can be classified in several ways; the main classification is based on their chemical nature and the functional groups they present. Within this classification are the catecholate, a functional group that plays an important role in the stability of complexes between siderophores and metals. These can be found in different species of bacteria and cyanobacteria.[47]

On the other hand, there are other sources of materials that have also proven to be efficient and effective for the enhancement of the photo-Fenton process, such as humic acids (HA), which is a natural compound present in waters.[48] One of the properties of the HA, due to its molecular structure, is the complexation of metals, among them iron.[2]

These are organic macromolecules with a certain complexity, as they have different functional groups. These include carboxylic, carbonyl and catechol moieties, which can be used to simulate the effects of humic acid-like substances in different processes, as they can be considered model compounds.[49] Interestingly, there is a study that shows how iron complexed by humic acids could be the major reservoir of iron in the oceans.[50]
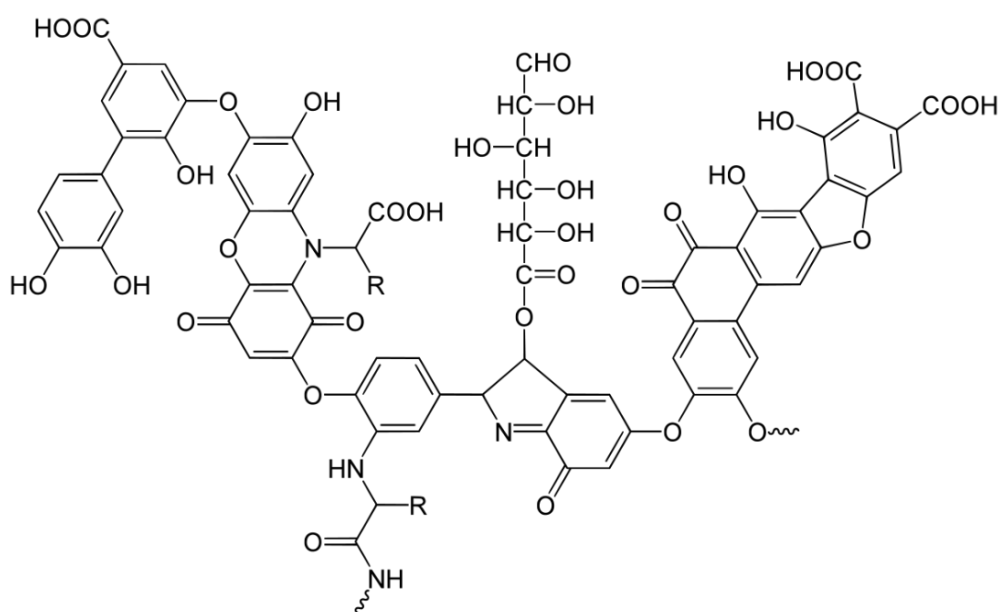
Figure 2. Structure of humic acids.

1.5.4.2 Homogeneous and heterogeneous Fenton reactions

Thus, within the Fenton processes, both the iron and the possible complexing agents can be added homogeneously, dissolving in the medium directly; or heterogeneously, adding the materials in solid form, which acts as a source for their subsequent action in the medium. Thus, chemical reactions can be divided into these two main groups, depending on the phase in which the reactants are

Homogeneous reactions are those in which the reactants are in the same phase and in solution. In heterogeneous reactions, on the other hand, the phases of the reactants are different and can react on the surface of solid materials, if applicable, or depending on the slow dissolution of the material in the medium.

Because of this, there are two major differences between these types of reactions:

- Physical separation: for the homogeneous case, this is not possible as all reactants are in solution. However, the main advantage of heterogeneous reactions is the possible separation and thus reuse of the different reagents or catalysts used in the process.

- Reaction rate: in homogeneous reactions, the reaction rate is higher because the reactants are in the same phase, facilitating the process. On the other hand, in heterogeneous reactions, the reaction rate is usually lower because of the phase change.

These are mainly the most common differences between the two types of reactions. Thus, depending on the time needed and the price of the reagents, one of the two cases is usually chosen if possible and comparable. [51]

2. OBJECTIVES AND HYPOTHESIS

The main goal of the study is to investigate HA as a possible complexant of iron at the photo-Fenton process to extend their efficiency to pH above 3. With that, it is tried to study if HA can be used as a complex agent in the process at values near to the circumneutral pH and in the presence or not of chlorides.

Thus, the specific goals of the study are:

1.   Study of humic acids substances as a complex agent on the photo-Fenton process at mild pH.

2.   Obtaining the pH value closest to the natural one in which the process can be applied efficiently.

3.   Study different sources of humic acids (homogeneous and heterogeneous) to compare their efficiency in the elimination of CECs at circumneutral pH.

4.   Check the effect of phosphates used commonly as buffers at photo-Fenton processes.

5.   Study the effect of chlorides on the process and whether HA is able to enhance the process in their presence.

6.   Corroborate the results obtained with the use of the electron paramagnetic resonance technique.

The goals described correspond to the objectives of the Sustainable Development Goals of the United Nations. In particular, the specific objectives referred to are:

- 6.   Clean water and sanitation
- 14. Life below water

Once established the objectives of the work, the hypothesis of the process, due to the previous works and information, as well as the conditions were chosen to perform the experiments, it is supposed that phosphate buffer and high values of pH will decrease the velocity of the degradation of CECs at Fenton treatment, showing worse results.

For the other part, the use of humic acids as a complexant will produce an enhancement of the process in homogeneous and heterogeneous phases. In this way, homogeneous experiments will get reach better results than heterogeneous results. Nevertheless, it is possible that bad results will appear in heterogeneous experiments because of the solubility of iron at values of pH above 3.

The effect of chlorides will show how they stop the process or affect it negatively. Nonetheless, low amounts of chlorides can enhance the process when it is performed at values of pH above 3. So it is possible, working in this scenario, to reach better results of degradation of CECs.

Finally, the use of electron paramagnetic resonance will confirm the formation of ·OH. These radicals are known for attacking organic compounds. With that, the presence of hydroxyl radicals will corroborate the results previously obtained during the experiments on the degradation of CECs.

3. MATERIALS AND METHODS

3.1 Solution

A mix of six contaminants of emerging concern (CECs) was used as a target solution. These contaminants were acetaminophen (AZMF), acetamiprid (ACP), amoxicillin (AMOX), caffeine (CAF), carbamazepine (CBZ) and clofibric acid (CLOF); which present different origins and uses. All of them were added to a concentration of 5 mg·L^{-1} in the mix.

To classify them and their use, every CEC was observed:

- Acetaminophen (PPCPs): it is an analgesic, used as a pain reliever

- Acetamiprid (Pesticide): it is an insecticide (neonicotinoid)

- Amoxicillin (PPCPs): it is an antimicrobial, used as an antibiotic

- Caffeine (PPCPs): it is a stimulant

- Carbamazepine (PPCPs): it is an anti-epileptic drug, used as an anticonvulsant

- Clofibric acid (PPCPs): it is an antihyperlipidemic, used as a lipid regulator

All of them are organic compounds, formed by carbon chains, which present a typical structure made by a ring with different functional groups such as methyl, carboxylic, etc. It can be seen in the figure below:
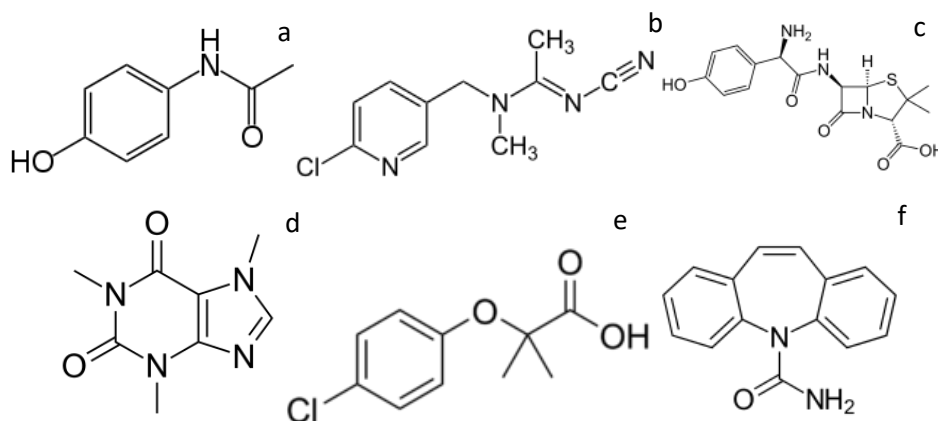

Figure 3. Structures of acetaminophen (a), acetamiprid (b), amoxicillin (c), caffeine (d), clofibric acid (e) and carbamazepine (f)

As discussed above in point 1. Introduction, their degradation study is very important due to their actual presence growth at wastewaters. How they can not be treated at WWTPs, they pass to the aquatic environment, making their presence in natural waters an important problem. Among all the problems that CECs create in the environment, the main ones are the development of antibiotic-resistant bacteria; some products that easily enter the food chain because they are lipophilic, like personal care products; possible health issues caused by the absorption of endocrine disruptors, troublemaking the normal functions of the body; the effect of some pesticides that causes hormone disruptions…

3.2 Chemicals

Some different chemicals were used to realise the experiments and control their parameters. In order to control the pH of the solution, sulfuric acid (H$_2$SO$_4$) 96% (Reag. Ph. Eur.) for analysis, ISO from PanReac AppliChem was used as an acid compound to regulate their value. Their choice was because chlorides have an effect on the process that is going to be studied. So the use of HCl as an acid compound is not a good option. Also, sulphates do not have an effect on the photo-Fenton process; this is what is the best choice. To realise the process, a solution of 0'1M of sulfuric acid was used.

For the other part, sodium hydroxide (NaOH) pellets for analysis, ACS, ISO from PanReac AppliChem was used as a basic compound. Like with the acid, a NaOH 0'1M solution was prepared to control the pH of the solution, mostly at the initial steps of the experiments.

As a source of iron(II) (Fe^{2+}), sulphate 7-hydrate ($FeHSO \cdot 7H_2O$) pure, pharma grade by AppliChem Panreac was employed. The concentration used to perform the experiments was 5 mg·L^{-1}. Due to the low volume of the experiments and the low concentration of Fe^{2+} needed, a concentrated solution of iron was prepared, adding it to the mix 10 minutes before each experiment. It was prepared each day, because iron(II) suffers oxidation into iron(III) when it is diluted in water because of the oxygen present in it.

For the iron complexation study, humic acids, supplied by Sigma-Aldrich, were used as a complexing agent. Based on previous studies.[52] the concentration used for this purpose was 10 mg·L^{-1}. In this way, results obtained can be compared as well as reliable due to the conditions previously studied and contrasted in other works. [53]

To complete the process, hydrogen peroxide was added to the mix. Hydrogen Peroxide 30% w/v for analysis was supplied by AppliChem Panreac. Stoichiometric value of CECs was used; what is the value of H_2O_2 needed to oxidize all the CECs present in the mix completely. It is known that hydrogen peroxide loses concentration over time so, to control the concentration of the solution of H_2O_2 of 30% w/v, it must be measured when it is necessary to use it, and the bottle has been opened sometime before. Thus, in order to prepare it and obtain the exact peroxide concentration, an absorbance study was carried out. For this, a known dilution of peroxide was prepared in Milli-Q water and its absorbance was measured at 240 nm. It is necessary to know that for a correct measurement, the absorbance value must be less than 1. Otherwise, the signal of the equipment may saturate and not show a correct value.

In order to quantify H_2O_2 concentration, the Lambert-Beer equation was used:

$$A = c \cdot b \cdot \varepsilon \qquad (4)$$

A = absorbance value of the sample

c = concentration of the solution (M)

b = cuvette path length (cm)

ε = molar extinction coefficient (M^{-1}·cm^{-1})

Thus, knowing the last measured molarity of the hydrogen peroxide bottle (8'8 M) and the parameters necessary to obtain the absorbance values as shown in equation 4, it was calculated that a dilution of 1:400 of the initial concentration was necessary.

Once the dilution was prepared, the absorbance analysis of the sample was performed. In this case, for 240 nm, the absorbance value was 0'89334. Hence, with the use of equation 4 and the value of the molar extinction coefficient ($\varepsilon_{H2O2,240nm}$ = 43'6 M^{-1}·cm^{-1}), a current molarity value of 8'2 M hydrogen peroxide was obtained.

On the other hand, the stoichiometric peroxide value necessary to eliminate the set of CECs from the problem solution was calculated. Knowing the reactions between each CEC and the hydrogen peroxide, a concentration value of 146'16 mg·L^{-1} of H_2O_2 was obtained, which must be added to each experiment. Due to the low amount of peroxide needed and the small volume of the sample treated in each experiment, a 0'82 M peroxide solution was prepared. Thus, for 50 mL of test solution, the addition of 262 µL of calculated and prepared hydrogen peroxide was necessary.

Finally, two phosphate buffers were used to maintain the pH stability during the experiments. Because experiments were performed at two different pH values, 5'0 and 6'0, each buffer had to be accurate for each pH value. For that, $H_2PO_4^-$ and HPO_4^{2-} salts were used.

3.3 Experimental conditions

The solution was made in all cases with Milli-Q water (distilled water (DW)). This water is water purify and ultrapure, widely used in experimentation processes. This type of water is used as a dissolvent to eliminate all the possible interferences with inorganic or organic compounds and salts that can be present in tap water. With that, the study of the reactions and the mechanism of each experiment is easier to follow, due to the total interaction only between the compounds that have been added. So, it is possible to have more representative results of what is happening at each moment of the experiment.

In order to see the effect of the photo-Fenton process at mild pH, all the experiments were performed at an initial pH of 5'0, near the circumneutral. For this, NaOH and H_2SO_4 0'1 M were used as a base and acid compounds to regulate it. The value of pH was measured with a pHimeter before and after each experiment, and it was checked.

To obtain representative results, three experiments were conducted in each condition. In this way, all the results are corroborated, being reliable and representative. So, graphics were represented with their error bands thanks to the use of the program 'Origins'.

Looking at the different experiments carried out, depending on the iron and humic acid status, these can be divided into two main groups. On the one hand, those experiments were performed in a homogeneous way. On the other hand, those experiments in which nanoparticles of magnetite were used as a source of iron and complexing agents, in a heterogeneous way.

3.3.1   Homogeneous experiments

In order to carry out the different experiments, some steps were followed to have representative and comparable results. All the experiments were performed at pH_0 5'0, to study the effect of mild pH on the photo-Fenton process as is said in the introduction. In some cases, a phosphate buffer of pH 5'0 was used to try to maintain the pH value stable during all the experiments, due to it goes to acid values because of the precipitation of iron and the formation of carboxylic acids. In some cases, it was worked without controlling it (this is, without buffer). In all the experiments pH was measured at the beginning and end.

The concentration of CECs present in the mix was 5 mg·L^{-1} each one. Also, the concentration of Fe^{2+}, needed to complete the Fenton cycle, was 5 mg·L^{-1}. When it was needed, 10 mg·L^{-1} of humic acids was added to the mix, and a stoichiometric value of CECs was used to know the needed amount of hydrogen peroxide, in this case, 146'16 mg·L^{-1}. [54]

For the study of the effect of chlorides in the photo-Fenton process, NaCl was used as a source of chlorides. For this purpose, two different concentrations were prepared: 1 g·L^{-1}, to simulate waters with low salt concentrations and to observe the effect of small amounts of chlorides in the medium (LSW), and 30 g·L^{-1}, to simulate marine waters since the average salt concentration in the sea is around this value (HSW).

Experiments were performed at an open glass, in a volume of 50 mL. A solar simulator was employed as an irradiation source. 340 nm filter was used to eliminate UV light, correctly simulating the sunlight. During all the processes, magnetic agitation was used.

For the photolysis experiments were carried out in 3 hours, taking samples at 1'5h. It is known that it is a slow process, to check their effect on the degradation of CECs. About the photo-Fenton process, 30 minutes experiments were performed, taking ten samples, in times: 0, 0'5, 1, 1'5, 2, 3, 5, 10, 15 and 30 minutes.

3.3.2   Heterogeneous experiments

Magnetite nanoparticles were used as a source of iron. Also, magnetite nanoparticles covered by HA were used as a source of iron and HA in the case where it wants to be seen the effect of the organic matter. All these nanoparticles were synthesised and characterised by N.P.F. Gonçalves et al. [55] It is possible to see all the characteristics of these materials in their work.

An initial pH of 5'0 was used to compare the effect on the heterogeneous matter with the homogeneous experiments. A volume of 50 mL was checked as in the case of the homogeneous study experiments. The same conditions were used for the pH control and peroxide addition. Moreover, the experiments were also

carried out under the same conditions and in the same solar simulator. Thus, experiments were carried out for 30 minutes, taking six samples, at 0, 2, 5, 10, 15 and 30 minutes.

3.4 Experimental procedure

As a source of irradiation to perform the photolysis and photo-Fenton experiments a Solar box from CO.FO.ME.GRA. Milano was used as a solar simulator. Experiments were carried out inside the simulator, opening the door only for taking the samples needed. A 340 nm filter was used to eliminate all the possible radiation below these values.

Figure 4. Solar box CO.FO.ME.GRA: and experimental procedure.

Sample preparation was the same in all cases. The mixture with the six contaminants was prepared at least one day in advance so that all the CECs were properly dissolved. This was not a problem as they were found to be stable in water and the mixture could be stored without any problem. In the case of the use of humic acids as a complexing agent, their addition to the mix was carried out in the same way, in order to obtain a correct dissolution of these.

On the other hand, the addition of iron was carried out during all the experiments 10 minutes before irradiation, in order to ensure similar conditions in all cases. The initial pH of the medium was adjusted prior to the addition and adjusted again, if necessary, after the addition of iron. Once the 10 minutes had elapsed, the hydrogen peroxide was added to the sample at the same time as the irradiation was started, taking this moment as the start of the experiment. It should be noted that the initial sample for each experiment was taken just before the addition of hydrogen peroxide.

The experimental process for sample extraction was similar for both homogeneous and heterogeneous experiments. Only one notable difference appears during this process, which is the use of a filter in the case of the use of heterogeneous materials since the presence of solids in the samples could damage the equipment used for the analysis. The filter used was of PTFE, 45 μm.

Thus, the analysed samples had a volume of 1 mL in total. Since the photo-Fenton process is based on the generation of hydroxyl radicals, which are very reactive, it is necessary to eliminate them once the samples are taken each time so that they do not continue to eliminate the CECs. For this purpose, methanol is used as a radical scavenger. The ratio was 1:2, so 0'33 mL of methanol was added to each vial, while 0'66 mL of samples were taken.

Finally, at the end of each experiment, the pH of the medium was measured. In this way, the variation of the pH value during the 30 minutes of the experiment was studied, in order to observe different behaviours in the medium depending on the type of complexing agent used or the nature of the complexing agent.

3.5 Analytical equipment

3.5.1   Spectrophotometer

Absorbance is based on the linear relationship between the amount of electromagnetic radiation per molecule of a compound and its concentration. In this case, it was used to measure the concentration of peroxide necessary for its use, as well as to find the maximum absorbance of each contaminant. This search for the maximum was done in order to set the wavelengths where the degradation of the CECs could be followed correctly. The test tube material used was quartz, as it does not present any interference at the selected wavelengths, which ranged from 200 to 300 nm.

For this study, the equipment used was the Hitachi UH 5300. This equipment offers a choice of wavelengths between 190 and 1100 nm and works with a xenon flash lamp.

Figure 5. Spectrophotometer UH 5300 Hitachi.

3.5.2   High-performance liquid chromatography (HPLC)

In order to follow and study both the elimination of the six selected CECs, as well as the possible appearance of certain intermediate compounds, the liquid chromatography technique was used. Due to the column employed, the C18 column, this equipment works in the reverse phase. It works thanks to the specific interactions between molecules of each sample with two phases: a fixed phase that is in the column and a mobile phase that flows through the column. The mobile phase is a mixture of two or three liquids: one organic, which would have a high polarity, as methanol or acetonitrile, and the other inorganic, which would have a low polarity compared to the former, as formic acid 10 or 100 mM. Depending on the polarity of the molecules in the solution, the proportions of these liquids vary.

In the case of the present work, the column used contains silicate groups functionalised with 18-carbon alkanes. Therefore the non-polar compounds will have a high affinity for the stationary phase compared to the polar ones. For that, because there are six different compounds in the mixture, a gradient programme will be carried out where the percentages of the eluents will vary during the measurement. This programme was:

Table 1. Gradient programme used for the HPLC.

Time (min)	% Acetonitrile	% Formic acid 0'01M	Flow (mL/min)
0	10	90	0'4
2	10	90	0'4
20	100	0	0'4
22	100	0	0'4
24	10	90	0'4
27	10	90	0'4

This ratio is used because the molecules to be worked with are mainly aromatic organic compounds, which have low polarity values. Therefore, being acetonitrile the component that represents the medium-low polarity phase, it will be in the majority in the mobile phase to favour the interaction with this type of compound. In this case, the model used to carry out this monitoring was the Agilent 1200 series HPLC system.

Figure 6. Agilent 1200 series HPLC system.

3.5.2.1 Absorbance of CECs

To choose at which wavelength the HPLC detector should obtain the signals of each CEC, an absorbance study was performed on the group of selected pollutants. This process was carried out to observe at which wavelengths each one absorbed, and to select the maximum wavelength of every pollutant.

Thus, a solution with a concentration of 5 mg·L^{-1} on Milli-Q water of each contaminant was made, to work on the concentration at which the degradation experiments will be carried out. Subsequently, an absorbance scan was performed from 200 to 800 nm.
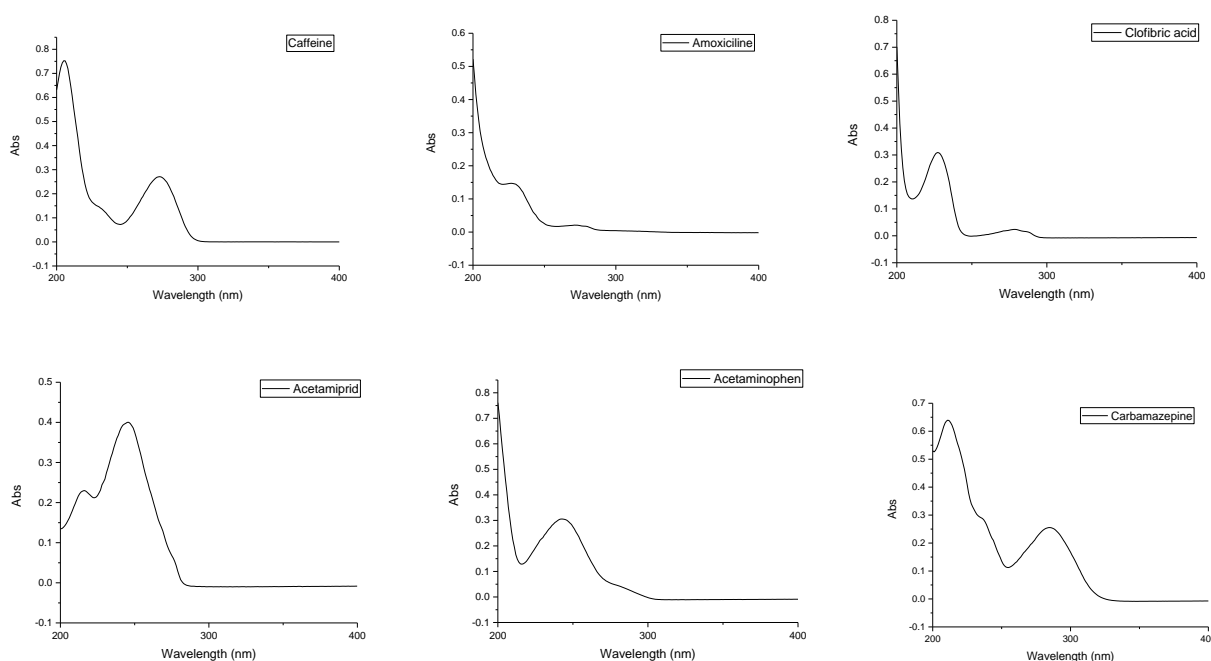

Figure 7. Absorbance spectres of caffeine, amoxicillin, clofibric acid, acetamiprid, acetaminophen and carbamazepine.

As can be seen, each contaminant has an absorbance maximum between 200 and 300 nm. Since HPLC allows detections at different wavelength values at the same time (because they have a photodiode detector), four values were chosen, depending on the pollutant to be followed. Thus, the values selected were:

- 210 nm: amoxicillin and caffeine.

- 215 nm: carbamazepine

- 220 nm: clofibric acid

- 240 nm: acetaminophen and acetamiprid.

In this way, the different HPLC detection values were established. Consequently, the respective data were noted for each contaminant value depending on this value, to ensure a correct detection and monitoring of their values.

3.5.3   Electron paramagnetic resonance (EPR)

Electron paramagnetic resonance (EPR) is a research technique applied to any molecular system that includes a part containing unpaired electrons and therefore exhibits a net magnetic moment.

This technique makes it possible to know whether an ion has a valence with unpaired electrons or whether the sample consists of a single paramagnetic compound, or to make a detailed study to obtain information on the symmetry and/or electronic distribution of the paramagnetic ion relative to the atoms forming the crystalline field seen by the ion, as is often the case with single-crystal specimens. The same paramagnetic entity can give completely different spectra if any of the ligands are changed, a phenomenon that is assumed to occur in a solid sample dissolved in different solvents.

As in the previous case, if a solid sample is dissolved in different solvents, it is expected that the same paramagnetic entity can give very different spectra. The applications of EPR are diverse, and it can be used in different fields of research in geology, medicine, chemistry, physics, etc. Due to its non-destructive nature and its wide versatility, it is a perfect complement to other analytical methods, providing valuable dynamic and structural information. Unlike other techniques, it can be used in the evolutionary study of physical-chemical processes without affecting their development.

For the case study, thanks to this technique it is possible to observe the presence of hydroxyl radicals in the medium. Since these are responsible for the elimination of CECs, it is important to know whether they are produced during the process, as well as in what quantity. For that, EPR spectra were obtained at room temperature. For that, a Bruker ESP300E spectrometer was used. Samples were taken in quartz capillary tubes, for their measurement. Finally, DMPO 17 mM was added to the sample before taking each one.

In this way, by means of the intensity value presented by the equipment in each experiment, it is possible to compare under which conditions more ·OHs are produced. Finally, thanks to these data it is possible to corroborate or disprove if the information agrees with the values of CECs elimination studied thanks to the use of HPLC. The degradation of CECs is due to the interaction of the organic compounds with ·OH so with the production of hydroxyl radicals, it is possible to see if the results present logical results. For the other part, it can be seen under which process conditions this generation is higher or lower.[56]

Figure 8. Bruker ESP300E spectrometer.

3.6 Experimental design

In order to have a global view of all the experiments performed, the total experimental design is shown. Depending on the nature of the complexing agent and the iron source, two main groups of experiments were carried out: humic acids and iron dissolved homogeneously or heterogeneously.

Within the homogeneous experiments, firstly, several control and initiation experiments were carried out, such as photolysis and the study of the effect of the buffer on this process. For this, photolysis was carried out at different initial pH values (5'0 or 6'0) and with the presence or absence of buffer.

Subsequently, the effect of the buffer on the photo-Fenton process was studied. Thus, the experiments were carried out at pH05, both with and without the presence of the buffer. Once the buffer effect was observed, the comparison of the photo-Fenton process with and without the presence of humic acids at pH_0 5'0 and pH_0 6'0 was carried out. In this way, it is intended to observe the effect of pH on the process, as well as the presence of the complexing agent in the process.

Once the process data were obtained with the reagents in a homogeneous state, magnetite nanoparticles coated or not with humic acid were used to observe the degradation of the CECs when they were present in a heterogeneous state. In this way, the data obtained for each process were compared.

Once the comparison had been made and the effect of each type of material had been studied, the effect of chlorides was studied. For this, the experiments were carried out homogeneously on two types of saline media: 1 g·L^{-1} of NaCl, to simulate wastewater that can present low concentrations of salts, named low salinity water (LSW), and a concentration of 30 g·L^{-1}, to simulate seawater, named as high salinity water (HSW).

Finally, using the Electron paramagnetic resonance (EPR) technique, the generation of hydroxyl radicals was observed during the process depending on the medium in which the treatment was carried out (DW, LSW and HSW). For this purpose, catechol was used as a type complexing agent to replace humic acids. This was because catecholate is part of the functional groups of humic acids. In this way, we tried to obtain in a clearer and more detailed way how they help in the photo-Fenton process thanks to the number of radicals generated during the process both with and without the presence of complexing agents in the medium.

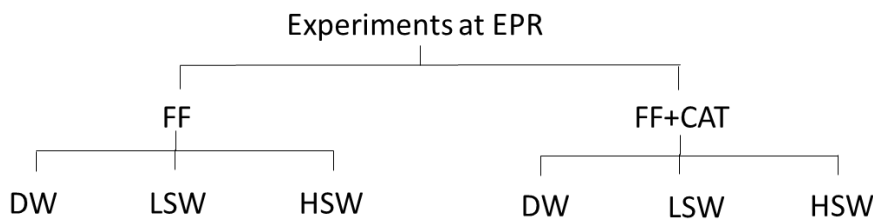Thus, schematically, the total number of experiments carried out was as follows:
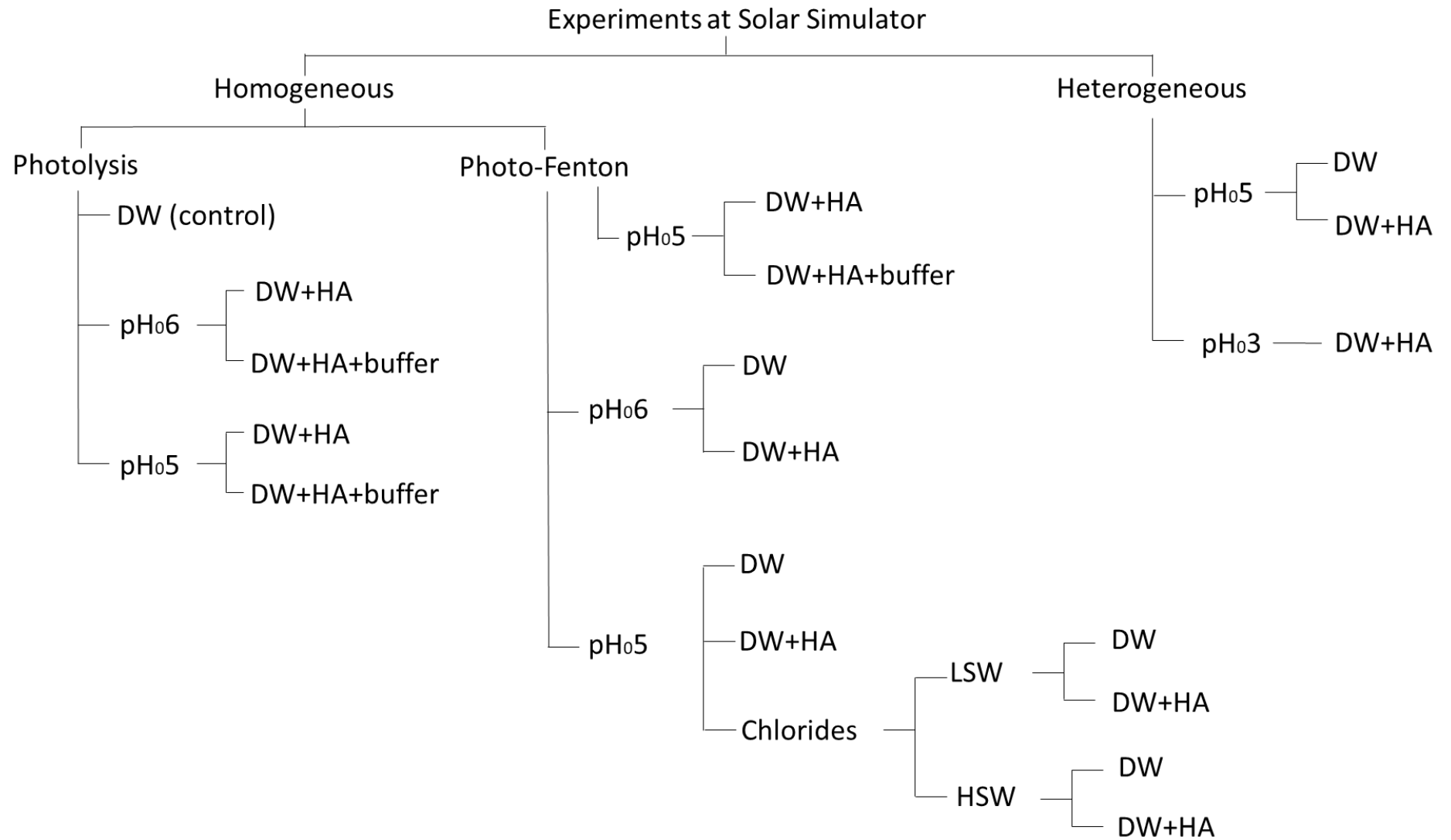

Figure 9. Scheme of EPR experiments.

Experiments at Solar Simulator

Figure 10. Scheme of experiments done at Solar Simulator.

4.   RESULTS AND DISCUSSION

4.1 Blank experiments

4.1.1   Photolysis experiments

In the first step**,** photolysis experiment was performed. This was done to explain how simulated solar light affects the process. The number of pollutants that are able to eliminate, only with the energy of the simulated solar light, was followed. Also, this experiment was used to determine if the solution is stable under the conditions of the solar box due to its geometry and how it works. For that, the solution was studied in a three hours irradiation experiment. Three samples were taken: minute 0 (initial), 90 minutes and 180 minutes (end of the experiment). The experiment was carried out at Milli-Q water and at natural pH.
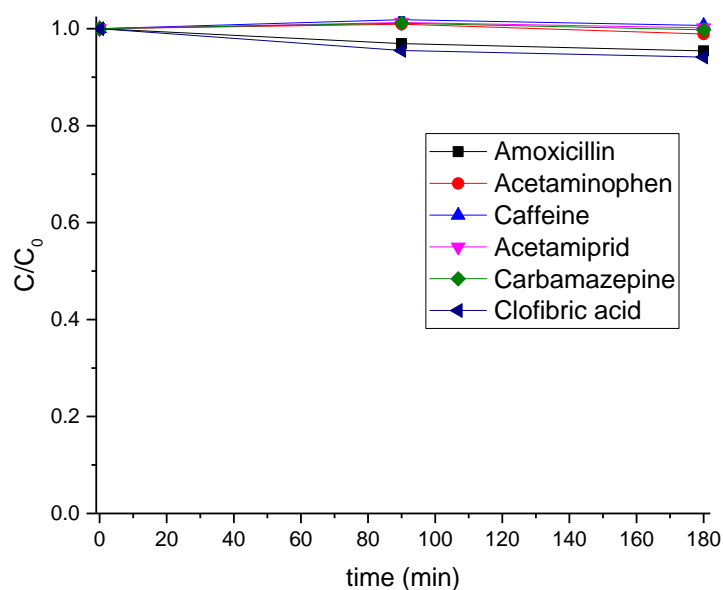

Figure 11. Photolysis experiment of CECs at natural pH.

As it can be seen, the solution presented that all CECs are photostable. Only clofibric acid and amoxicillin showed some degradation, less than 10% in each case after three hours of irradiation.

Seeing these results, some other photolysis were studied. The principal goal is to observe the differences between work at pH_0 5'0 or pH_0 6'0, because it is known that the process is less effective when the pH value increases.[2] Otherwise, how can affect the presence or not of phosphates for each one was studied too. Since the common buffers used in the process are made with phosphates and these have previously been observed as negative compounds in the presence of iron, it is assumed that they will not show any change in the photolysis processes due to there is no iron present in this type of reactions.

For the other part, the stability of HA due to UV-vis radiation, as well as its interaction with the CECs present in the solution, was studied. For that, two values of pH were studied as told above. First, due to their previous use in some experiments[57], the study at pH_0 5'0 was carried out like a principal pH value (Figure 12a and 12b). Else, because of their more approach to the circumneutral pH, the value of 6'0 was studied too (Figure 12c and 12d).
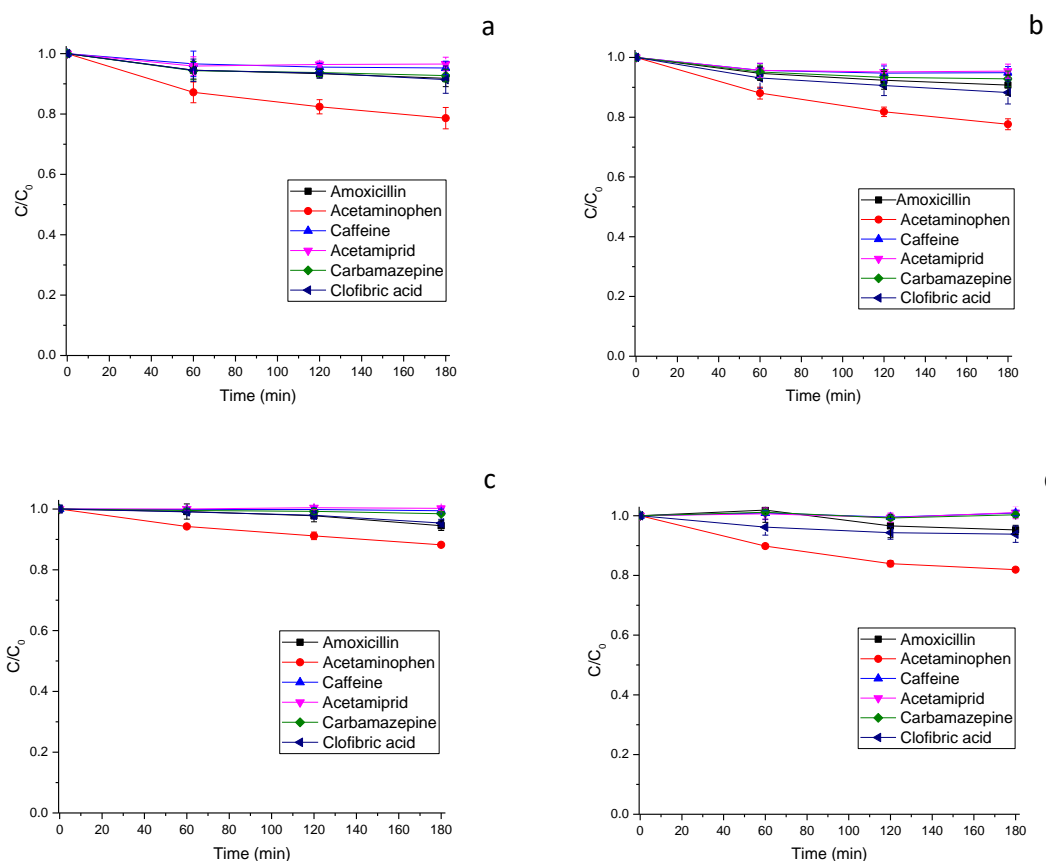
Figure 12. Photolysis experiments of CECs with HA at pH 5'0 with phosphates (a), pH 5'0 without phosphates (b), pH 6'0 with phosphates (c) and pH 6'0 without phosphates (d).

As it can be seen, the principal difference between the presence (Figure 12) and absence (Figure 11) of humic acids in the mix is the amount of acetaminophen eliminated in each case. This is because of the interaction between the HA and this CEC, which seems to have a big affinity to the molecule, eliminating it first and in a big measure.

For the other part, it is not possible to see differences between work at pH_0 5'0 or 6'0 due to the presence of phosphates in the mix. This is because they have not affected the process in the conditions chosen.

4.1.2 Study of iron stability

Once the photolysis blanks were performed, the first step before doing the photo-Fenton process was to study the stability and precipitation of iron in the water. It is known that the species of Fe(II) and Fe(III) are stable at acid pH, but suffer precipitation if the medium presents a value of pH higher than 3. This is one of the reasons why photo-Fenton only works correctly at pH values under 3.

To check the solubility of iron at the pHs used, many solutions of Fe(II) and Fe(III) were made at pH 5'0 and 6'0. The solutions present concentrations of 5 and 1 mg·L^{-1} of iron, to see if there are some differences between the amount of iron present in water too.

These samples were left at rest for three days in obscurity and, after it, two checks were made. First, a first sight, the solutions were observed. Only four of them present precipitation, those that have a solution of Fe(III) with an amount of 5 mg·L^{-1}.

To corroborate it and have representative results, an absorbance study was done. Precipitation always presents absorbance at values between 700 and 800 nm so, those samples which present this effect can be checked. With that, all the samples were studied with the hypothesis that only those with Fe(III) at 5 mg·L^{-1} in solution will show this effect.
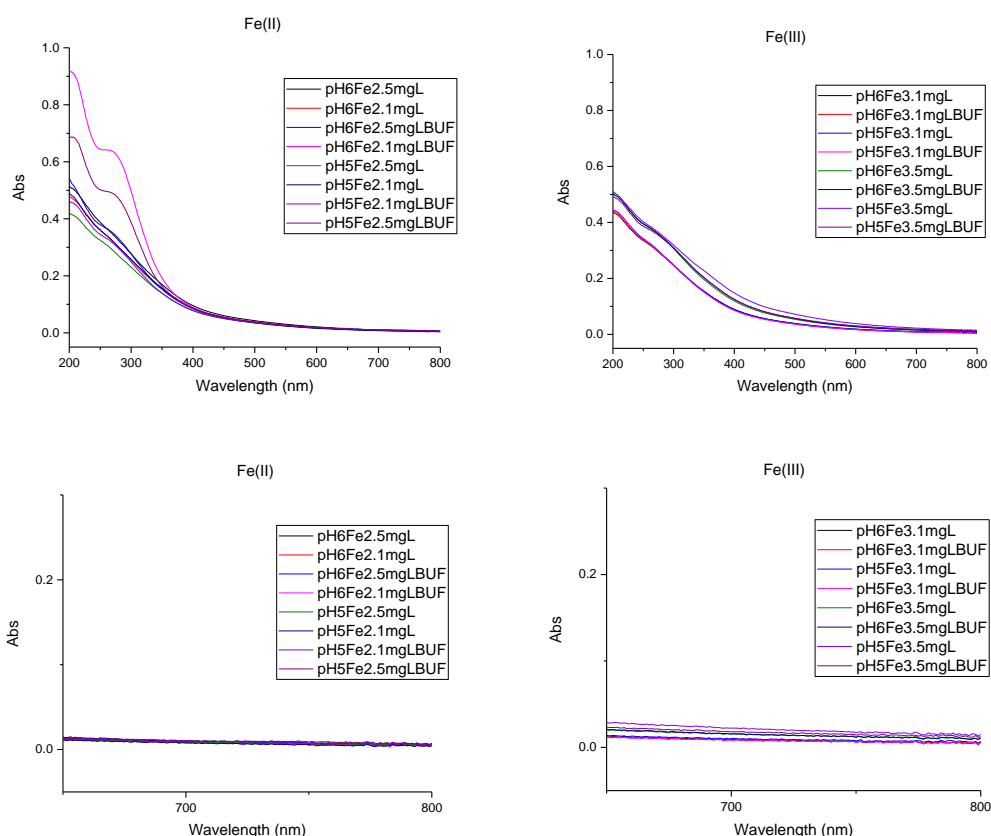
Figure 13. Absorbance spectres of different solutions of iron (II) and iron (III) at different conditions.

As can be seen, only the solutions with 5 mg·L^{-1} of Fe(III) present an absorbance at intervals between 700 and 800 nm. It corroborated the previous study made at first sight, so, thanks to this, it was chosen to perform the experiments with Fe(II) due to their big stability, in comparison to Fe(III), at near to the circumneutral pH. Also, all the experiments done in other works with complexants have been performed with Fe(II) so, thanks to that, it is possible to compare it.

4.2 Photo-Fenton process

Once observed the photolysis effect on the CECs, and the stability of Fe(II) in DW, the next step was the study of the solution with the use of the photo-Fenton process.

4.2.1   Study of phosphates effect at the photo-Fenton process

In the first step, the effect of the phosphates commonly used as a buffer in the Fenton and photo-Fenton processes were studied. As was informed before, previous studies made with phosphates show a negative effect on photo-Fenton processes due to they formed iron phosphates salts, precipitating the iron present in the mix.[2]

In this work, the experiments were carried out with the presence of humic acids as a complexant of iron, at pH$_0$ 5'0, and with the presence or not of phosphates to check it. A photo-Fenton experiment of two hours was carried out, taking different samples at different times. The number of phosphates added was 0'16 mM, being phosphates salts: $H_2PO_4^-$ and $HPO4^{2-}$.
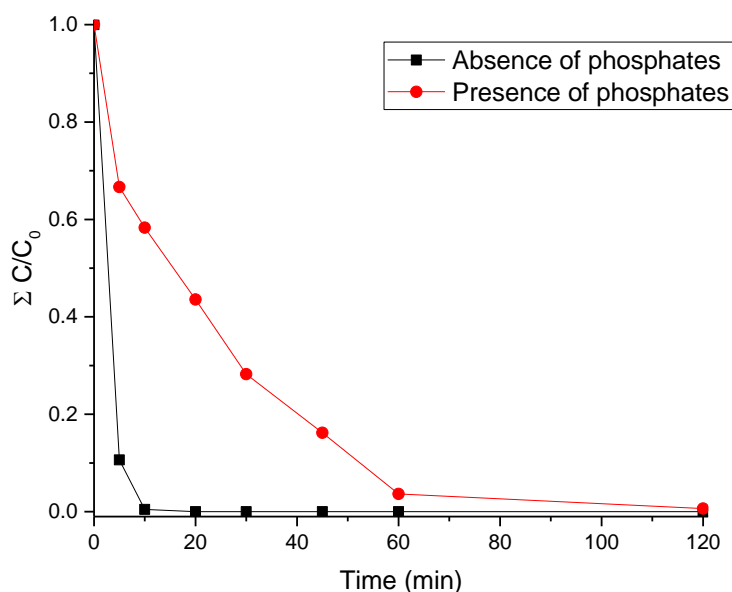
Figure 14. Effect of phosphates in the degradation of CECs at photo-Fenton process.

As it can be seen, the presence of phosphates makes the reaction of elimination of the sum of CECs gets worse to a large extent. While without them CECs are eliminated in 10 minutes, with the presence of phosphates only near to 30% of the total amount of them are eliminated, being completely threatened after 2 hours of irradiation.

To determine if this effect is due to the presence of the phosphates or the possible effect buffer of them, the pH of the solution was checked at each experiment before and after the irradiation. If phosphates would make the buffer effect, it is supposed that pH can not change, and always will stay at the value of 5'0, while without it, it is studied and known that its value decreases to values between 3'0 and 4'0, near to the photo-Fenton optimal pH, which is 2'8. Nevertheless, the values of pH indicated that the amount of phosphates added is not enough to do the buffer effect. It can not maintain the value of 5'0 during the experiment, having a lower value at the end of the experiment. The values reported were:

Without buffer:	Initial pH: 5'1	Final pH: 3'8
With buffer:	Initial pH: 5'2	Final pH: 3'9

For this reason, it is correct to say that the effect of the slow elimination of the contaminants is because of the presence of phosphates in the mix. It corroborates previous studies[2], that show how phosphates stop the photo-Fenton process, as it happens in the work presented, due to the precipitation of iron, as was previously mentioned.

4.2.2   Study of different pH values

Once seen the bad effect of the phosphates commonly used as a buffer in the process, the effect of working at different initial pHs was studied. In the first step, two photo-Fenton processes without humic acids, at pH_0 5'0 and pH_0 6'0, were performed to have a reference to compare the results obtained. With that, it is possible to check the effect of the humic acids in the process, comparing it with its absence.
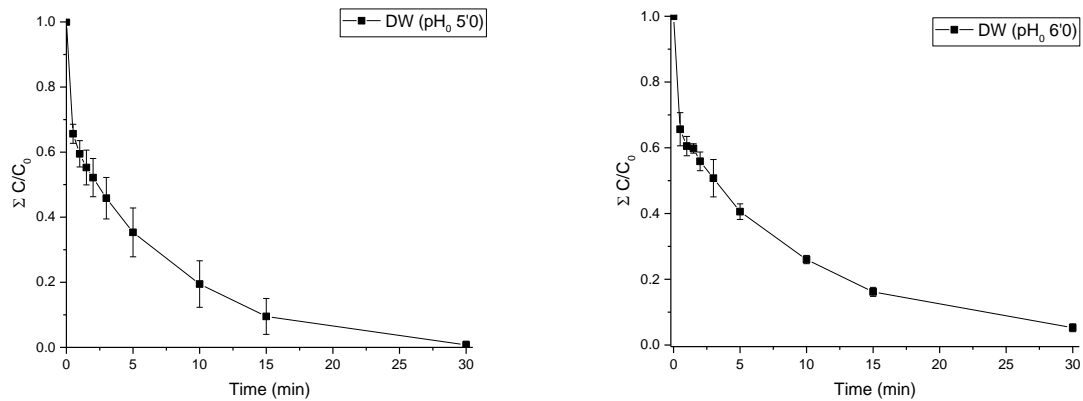
4.2.2.1 Photo-Fenton process: effect of pH

Figure 15. Degradation of CECs at photo-Fenton process at pH_0 5'0 and pH_0 6'0.

As shown in Figure 15a, the process presents an initial fast elimination due to work with Fe(II), because the process is starting to form a lot of highly reactive radical hydroxyls. Later, it presents their characteristic behaviour, eliminating around 50% of the total amount of CECs at the time of 2 minutes. After 15 minutes of irradiation, around 90% is eliminated and, finally, practically the total amount of them after 30 minutes of irradiation.

After this first study, the effect of pH was checked by performing the same experiment but at an initial pH value of 6'0. With that, it is tried to see how working near circumneutral values of pH can affect the elimination of CECs by the photo-Fenton process.

As shown in Figure 15b, at initial fast degradation of CECs occurs due to working with Fe(II), as it is explained in the previous case. The 50% of degradation is reached after 3 minutes of irradiation, showing a lower velocity on the process than working at pH_0 5'0. After 15 minutes of irradiation, more than 20% of CECs are eliminated, but after 30 minutes of irradiation it is not degraded the total amount of contaminants.

4.2.2.2 Photo-Fenton process with the addition of HA

After seeing the results of the photo-Fenton process at pH_0 5'0 and 6'0, humic acids was used to observe its effect as a complexant. Two experiments were conducted, at a value of pH_0 5'0 and 6'0, the same as the photo-Fenton process without any complexant.
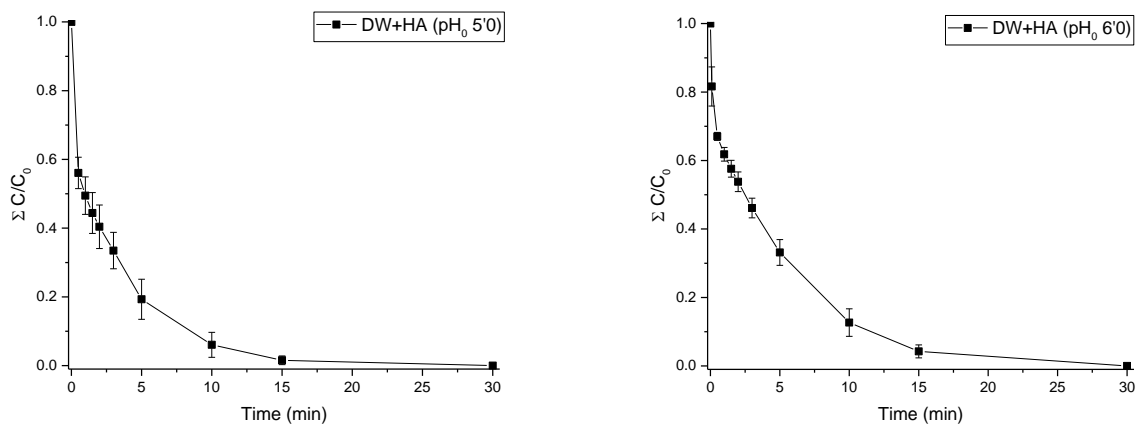

Figure 16. Degradation of CECs at photo-Fenton process at pH_0 5'0 and pH_0 6'0 in the presence of HA.

As can be seen in Figure 16a, at pH_0 5'0, 50 % of the sum of CECs was eliminated after one minute of irradiation. Furthermore, after 15 minutes of irradiation, CECs were eliminated from the mix, presenting a better result than the process without the presence of complexant.

Once studied the effect of the humic acids was at pH_0 5'0, and experiments were realised at pH_0 6'0. The main goal is to observe if it is possible to work at pHs near the neutral or circumneutral. In Figure 16b, the results have shown that the 50% of degradation of CECs was reached after 2 minutes of irradiation, remaining around an amount of 5% after 15 minutes and being eliminated after 30 minutes of it.

4.2.2.3 Comparation of all processes

With all these results, it is possible to compare the experiments realised. Hence, the effect of the complexant was studied, just like the effect of work at a pH near the circumneutral.
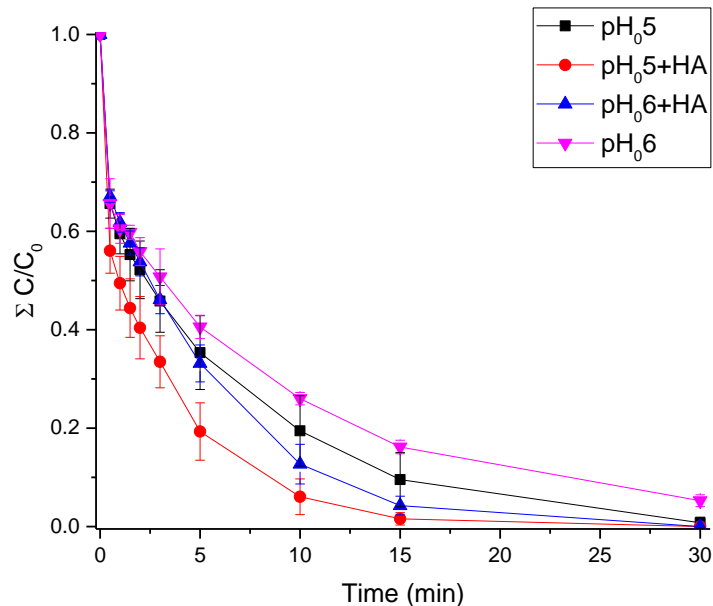

Figure 17. Comparation of the photo-Fenton processes at pH_0 5'0 or 6'0 with the presence or absence of HA.

As Figure 17 shows, the use of a compliant made the process works better and faster. The principal difference can be observed at the velocity that CECs were eliminated at the initial steps, making big differences after 5 minutes of irradiation, with a difference of 15% of the total sum of CECs eliminated. Also, the time at which the total amount of CECs is eliminated is a significant indicator. While without organic matter it occurs after 30 minutes of irradiation, with the use of human acids it is only needed for 15 minutes, rather, half the time.

Otherwise, the comparison between work at pH_0 5'0 or 6'0 shows how the effect of the pH value is an important variable that should be studied and checked. If the value of pH increases, the velocity of degradation of CECs decreases, having a big difference in velocity at first steps and being better after 10 minutes of irradiation, when it changes and becomes faster. Nevertheless, after 15 minutes the process is not able to eliminate all the contaminants if it is worked at pH_0 6'0, increasing the time needed to eliminate all of them to 30 minutes.

With all these results, on the one hand, it is correct to say that the use of humic acids as a complexant improves the process in a big way, reducing the time needed to eliminate the total amount of CECs to half in comparison with the photo-Fenton process and presenting a quick elimination of them at initial steps. On the other hand, increasing the pH of the solution to circumneutral values made the reaction goes badly due to the inactivation of iron at these more basic values. With all, the bests results are obtained with the use of humic acids as a complexant at a pH_0 5'0, eliminating the total amount of CECs present in the mix after 15 minutes of simulated solar irradiation.

4.3 Heterogeneous photo-Fenton process

Once see the photo-Fenton enhancement carried out by the humic acid as a homogeneous complexant, it seems interesting to study the behaviour of these components as heterogeneous complexants.

The use of heterogeneous materials as complexants have some advantages, and disadvantages. For one part, the possible reuse of it is the most important reason to use this type of material. Nevertheless, it is known that the velocities of reaction, comparing them with homogeneous materials, is slowly. So, for that, some different nanoparticles were developed in order to reach this knowledge.

First, experiments with the use of magnetite and magnetite covered with humic acid nanoparticles in DW at pH_0 5 were conducted. In these cases, it is not necessary to add iron due to it is provided by the magnetite present in nanoparticles. It is only needed to add the hydrogen peroxide before starting the experiments.
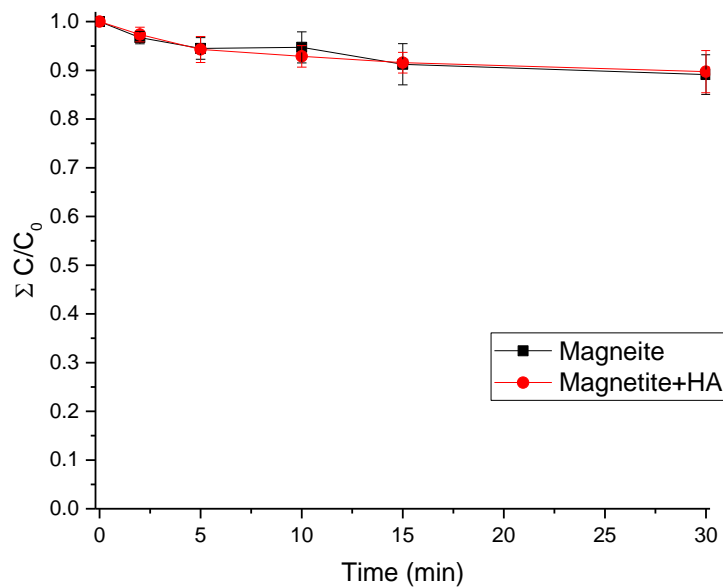

Figure 18. Behaviour of CECs at heterogeneous photo-Fenton process at pH_0 5'0 in the presence or absence of HA.

As it can be seen, the results show that there is not a relevant degradation of the sum of pollutants. Only 10% is eliminated, in the presence or absence of HA, after 30 minutes of irradiation.

Whether each pollutant is observed individually, only one present degradation. The acetaminophen is eliminated in 50% with the use of magnetite covered with humic acid (Figure 19). Nevertheless, this happens only in one of the six contaminants that the solution has, so it's not convenient to use the nanoparticles in the photo-Fenton process at circumneutral pH.
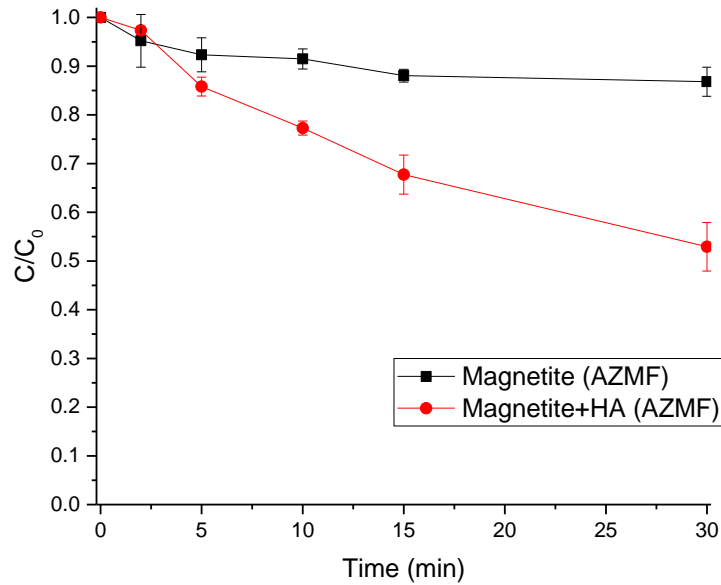
Figure 19. Behaviour of acetaminophen at heterogeneous photo-Fenton process at pH$_0$ 5'0 in the presence or absence of HA.

This is the same effect that occurs with photolysis (Figure 11). As it can be seen in the first experiment of humic acid as a homogeneous complexant, only acetaminophen presents an appreciable degradation when humic acid is added to the mix, verifying that the organic matter present in the nanoparticles is working correctly and has an effect on the process.

Nevertheless, the amount of CECs degraded is too low, and practically insignificant, which indicates that the nanoparticles are not efficient in carrying on this process. As it can be seen in figure 19, only the acetaminophen is eliminated when there are humic acids present in the mix. This shows how the nanoparticles are not able to degrade CECs at mild pHs, making the heterogeneous photo-Fenton process useless. Nevertheless, it is important to see how HA are able to improve the photo-Fenton process even when it is poor efficient.
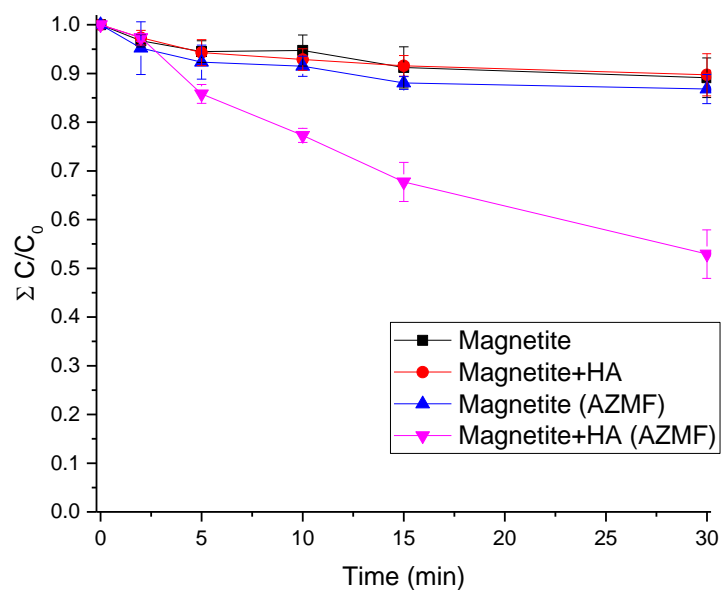

Figure 20. Comparison of the behaviour of CECs and acetaminophen at the heterogeneous photo-Fenton process at pH$_0$ 5'0.

These values can be explained for two reasons; first, as shown in work done by Nuno et. al.[52] it is possible to explain the results due to the solubility of iron (II) and (III) at different pHs. As it indicates, when the pH of the solution is near the circumneutral, the amount of Fe(II) and Fe(III) released in the solution is very low.

At pH_0 6'0, the amount present of iron in the solution is the same for iron (II) and iron (III) at times 0 and 3 hours, only less than 0.0025 mM. Therefore, at pH_0 5'0, the pH of work, nanoparticles are not able to release iron into the water matrix. Because of that, the solution does not present iron in solubility and the photo-Fenton process cannot work if it's performed at these pH values.

For another part, it is possible that the nanoparticles are oxidised. This can be possible due to they were prepared four years ago so, during all this time, it is possible that they suffer oxidation and, for that, do not work efficiently. Seeing the solubility of iron at different pH, at pH 3'0, the amount of iron (II) and (III) released in solution at time 0 is near to 0'007 mM, being of 0.01 mM to iron (III) and 0'022 of iron (II) after 3 hours. Also, at pH 4'0 these values decreased to 0'0025 mM at time 0 and less than 0'004 mM of iron (III) and near to 0'0075 mM of iron (II) after 3 hours.

So, to demonstrate if the nanoparticles are oxidised or the degradation obtained is because of the solubility of iron, an experiment with the nanoparticles of magnetite covered with humic acid (because they had better results than magnetite nanoparticles) at pH_0 3'0 was carried out. This was conducted because it is known that the nanoparticles work correctly at this value of pH, due to the iron released in the solution presents high levels of concentration.
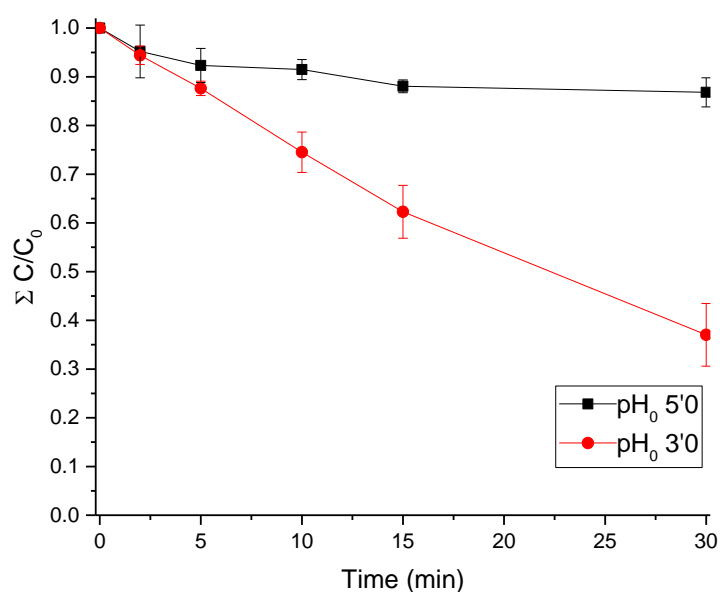

Figure 21. Behaviour of CECs at heterogeneous photo-Fenton process at pH_0 5'0 and 3'0.

Figure 21 shows how working at pH_0 3'0 a significant degradation of CECs is reached, having approximately a 60% of CECs degraded after 30 minutes of irradiation. Thus, it is confirmed that the nanoparticles work correctly at pH_0 3'0 and that it can be accepted the hypothesis presented. The problem is that Fe^{2+} and Fe^{3+} can do not release at pH near to the circumneutral, or they released in very low quantities and precipitated at the moment. The source of iron is magnetite nanoparticles. So, with this, the use of this type of heterogeneous material can not be used to perform photo-Fenton processes at values oh pH_0 5 or higher.

4.4 Chlorides effect

Once the study of the photo-Fenton process using nanoparticles had been carried out, and it was observed that its application is not possible in pH ranges close to neutral due to the low or null solubility of iron in the medium, it is proceeded to study the effect of inorganic ions, in this case, chlorides. For this purpose, the photo-Fenton process was carried out with the addition of homogeneous iron and humic acids.

First, the effect of chlorides in a mixture with Milli-Q water on the photo-Fenton process without the use of HA was studied. For this purpose, two different concentrations of NaCl were used as discussed in the Experimental section: LSW, presenting a concentration of 1 $g·L^{-1}$, simulating low-salinity water coming for example from wastewater; and HSW, with a concentration of 30 $g·L^{-1}$, to simulate seawater.
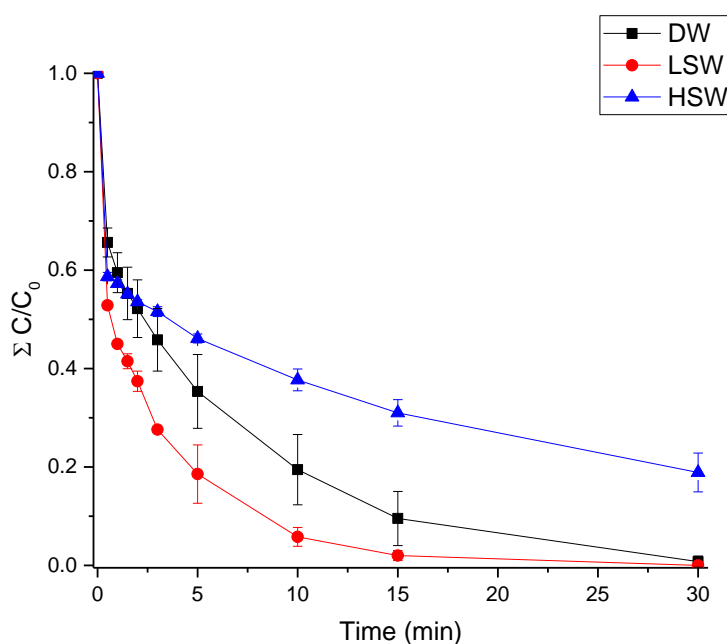

Figure 22. Degradation of CECs in the photo-Fenton process at different water matrices (DW, LSW and HSW) at pH_0 5'0.

As can be seen, the presence of a 30 $g·L^{-1}$ of chlorides in the medium presents a notable disadvantage in terms of the elimination of the CECs. The most noticeable differences begin to appear a few minutes after starting the process, with a difference of 10% after 5 minutes compared to the base photo-Fenton process, where CECs at HSW present a degradation of 55%, being of 65% on DW. This difference increases as the process progress, reaching 20% after 15 minutes (degradation of CECs of 65% on HSW and 90% on DW) and 20-25% after 30 minutes when they have been completely eliminated in the photo-Fenton process. Thus, after half an hour of irradiation, 25% of CECs remain in the HSW medium, whereas in the distilled water process all contaminants have already been removed. Hence, the effect of 0'5 M chlorides in the medium can be confirmed because chlorides capture hydroxyl radicals as they are highly present in the medium and prevent them from attacking the pollutants.

However, if the effect of the chlorides is observed when they are in low concentration, they manage to improve the process. This improvement occurs to a large extent in the first few minutes, with almost 17% more CECs being eliminated 3 minutes into the process, with a degradation of CECs of 55% on DW and more than 70% on LSW. After 15 minutes, the percentage of CECs removal was 95%, in contrast to the normal process which was around 90%. With that, it is clear that at LSW the elimination of CECs goes faster than at the photo-Fenton process in DW, having an enhance in it.

These data differ from previous studies, where the presence of chlorides in the medium has a negative effect.[58] However, this occurs when working at the optimum pH of the photo-Fenton process, which is 2'8. Chlorides are highly negative in the process at pH<3'0; however, as their value increases, this effect decreases and is less noticeable. It can be observed that in the presence of low chloride concentration the optimum pH

of the process changes to a pH value of 3'4. This is due to a change in the coordination sphere of the iron Fe^{3+}, changing the mechanism, thanks to the most important paper of species how $FeCl_2$ in the process. [57] Therefore, the presence of a low concentration of chlorides in the medium is able to improve the process thanks to the complexation of iron and the appearance of chloride radicals, which are much less reactive than hydroxyl radicals but help to eliminate CECs.[59]

Subsequently, the effect of chlorides in the medium was studied, but with the addition of humic acids as a complexing agent in the medium. In this way, it is tried to observe whether they are able to improve the process even in the presence of chlorides in the medium or, on the other hand, whether there is a reaction between them that changes their behaviour.
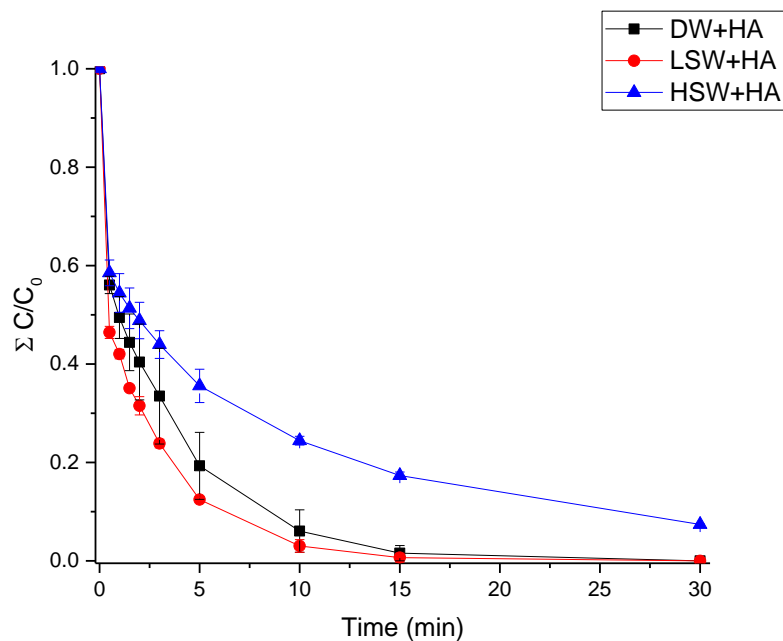

Figure 23. Degradation of CECs in the photo-Fenton process at different water matrices (DW, LSW and HSW) at pH₀ 5'0 with HA.

As can be seen, the order of the results is the same as in the previous case, with the removal of CECs being higher in LSW and lower in HSW. However, in this case, the difference between photo-Fenton in Milli-Q water and LSW decreases, and the total CECs are practically eliminated after 15 minutes in both cases.

In the case of HSW, the difference in CEC removal starts to become noticeable between 3 and 5 minutes, with differences of 10-15% lower removal rates. In this case, after 15 minutes of irradiation, 80% elimination is found, leaving around 10% of CECs when irradiation has been carried out during the 30 minutes of study.

With all these data, it is interesting to note the difference that appears between the use or not of humic acids as a complexing agent. In this way, it is possible to appreciate the effect of these together with the effect of chlorides, observing in a simpler way if they can improve the process in these media.
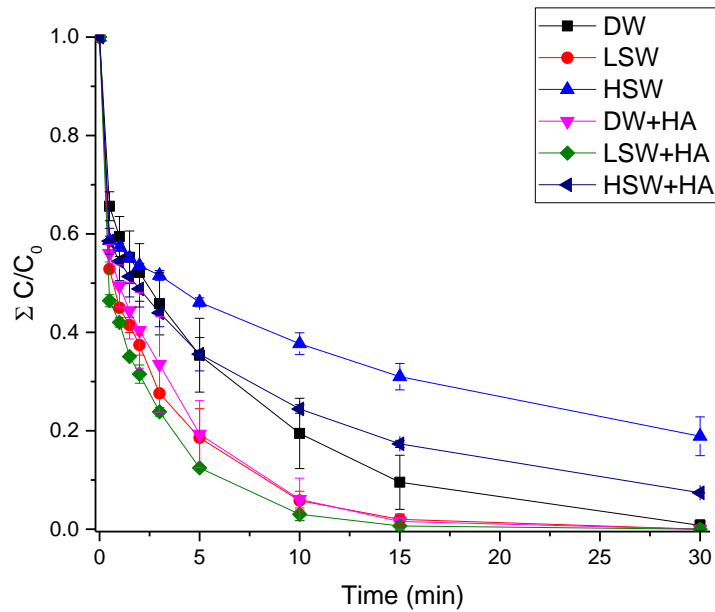
Figure 24. Comparison of the degradation of CECs in the photo-Fenton process at different water matrices (DW, LSW and HSW) at pH_0 5'0 in the presence or absence of HA.

As can be seen, there are various cases in which the process improves with respect to the base photo-Fenton process, while in other cases the elimination of CECs is slower. Among the processes that improve and present higher removal rates, when working in LSW medium, the results obtained are practically the same as when working in DW and the addition of HA. Together with their combination, the best results are obtained, presenting a slight improvement with respect to the presence of one of these two factors, increasing the degradation of CECs by approximately 5% after 5 minutes of irradiation, with an elimination of 87% of these. Thus, the presence of HA provides higher removal rates.

On the other hand, the presence of high amounts of chlorides in the medium, HSW, slows down the photo-Fenton process. However, the addition of humic acids to the medium manages to reduce this effect considerably, presenting elimination values more similar to the normal process. Thus, up to 5 minutes the values are the same, slowing down from this moment onwards, where at 10 minutes a difference of less than 5% appears, increasing to 7% at 15 minutes. Finally, after 30 minutes of irradiation, the CECs have been totally eliminated in the photo-Fenton process, while working in the HSW medium there are still about 20%, being less than 10% with the presence of HA in the medium.

4.4.1   pH study

On the other hand, a study of the pH variation in all cases was also carried out. Due to the fact that the experiments were carried out without the use of any buffer, the pH varies during the process, indicating this variation if there is a high or low activity in the process. Also, if it varies towards pH values closer to the optimum, better degradation results are possible due to this effect.

Thus, observing the initial and final pH values (after 30 minutes of degradation) within the photo-Fenton processes carried out, the following results were obtained:

Table 2. Values of pH at the beginning and the end of the photo-Fenton experiments at different water matrices (DW, LSW and HSW) in the presence or absence of HA.

Experimento	pH inicial	pH final
DW	5'0 ± 0'1	3'6 ± 0'1
DW+HA	4'9 ± 0'1	3'6 ± 0'1
LSW	5'0 ± 0'1	3'6 ± 0'1
HSW	5'0 ± 0'1	3'6 ± 0'1
LSW+HA	5'0 ± 0'1	3'8 ± 0'1
HSW+HA	5'1 ± 0'1	3'7 ± 0'1

As can be seen, they all have a similar variation. The photo-Fenton process is based on the elimination of the organic compounds present in the medium, thus forming carboxylic acids. These acids generate a decrease in the pH of the sample. Therefore, acidic pH values after the degradation process indicate oxidation of the CECs as is the case. On the other hand, this phenomenon may be due to the precipitation of the Fe^{3+} present, which precipitates as $Fe(OH)_3$, capturing three OH^- from the medium and causing the medium to become acidic.

However, looking at the degradation results of CECs, this result can be corroborated by the decrease in the pH value. This is mainly due to the formation of carboxylic acids, which appear due to the oxidation of the CECs as discussed above.

4.5 EPR study

Finally, to corroborate the studies carried out on the photo-Fenton processes, the action of the complexing agents and the effect of the chlorides, the EPR technique was used.[53] With this technique, the generation of hydroxyl radicals due to the interaction between iron and hydrogen peroxide was observed, with the variables of the use or not of complexing agents and the addition of chlorides. All the tests were carried out at pH_0 5'0, following the same experimental procedure as in the previous cases.

For this study, there was a variation in the use of the complexing agent. Because humic acids have many different functional groups capable of complexing iron, it was decided to use catechol as the type functional group to obtain clearer and more differentiated results. Thus, a concentration of 25 mg·L^{-1} catechol was used in the corresponding cases, following previous works.[54,57]

On the other hand, three different aquatic media were used for testing. These, as in the case of the photo-Fenton processes, varied the number of chlorides in each. Hence the media used were DW, LSW and HSW.
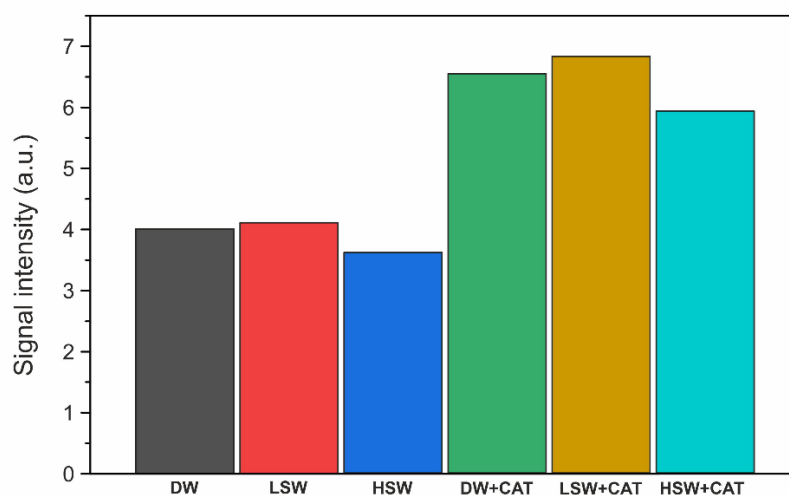
Figure 25. Signal of the generation of ·OH at different water matrices (DW, LSW and HSW) in the presence or absence of CAT at the minute 1 of the reaction.

As the figure shows, in a first study without the presence of catechol, the generation of hydroxyl radicals presents similar values in the first minute of the experiment. However, small differences are observed, coinciding with the degradation rates of the CECs in each medium.

Thus, the medium in which more ·OH is generated is LSW. This may be due to a part of iron complexation by chlorides, improving its stability in the medium and, therefore, the dissociation of H_2O_2 into hydroxyl radicals. With an almost similar but slightly lower intensity value is DW, and finally, the medium with the lowest ·OH generation is HSW. This is due to the very high presence of chlorides in the medium, which hinders the interaction between iron and hydrogen peroxide, thus producing a lower amount of radicals.

On the other hand, with the presence of catechol as a complexing agent in the medium, the generation of hydroxyl radicals is greatly increased compared to the processes without a complexing agent. This comparative increase was around 75%, therefore showing the significant effect of the use of complexing agents in the process when operating at pH_0 5'0. Also, the order of radical generation coincides with that without catechol, thus showing the positive effect of working with small concentrations of chlorides, which help to complex the iron to a small extent. Similarly, a high amount of chlorides reduces the generation of ·OH, due to the explanation given above.
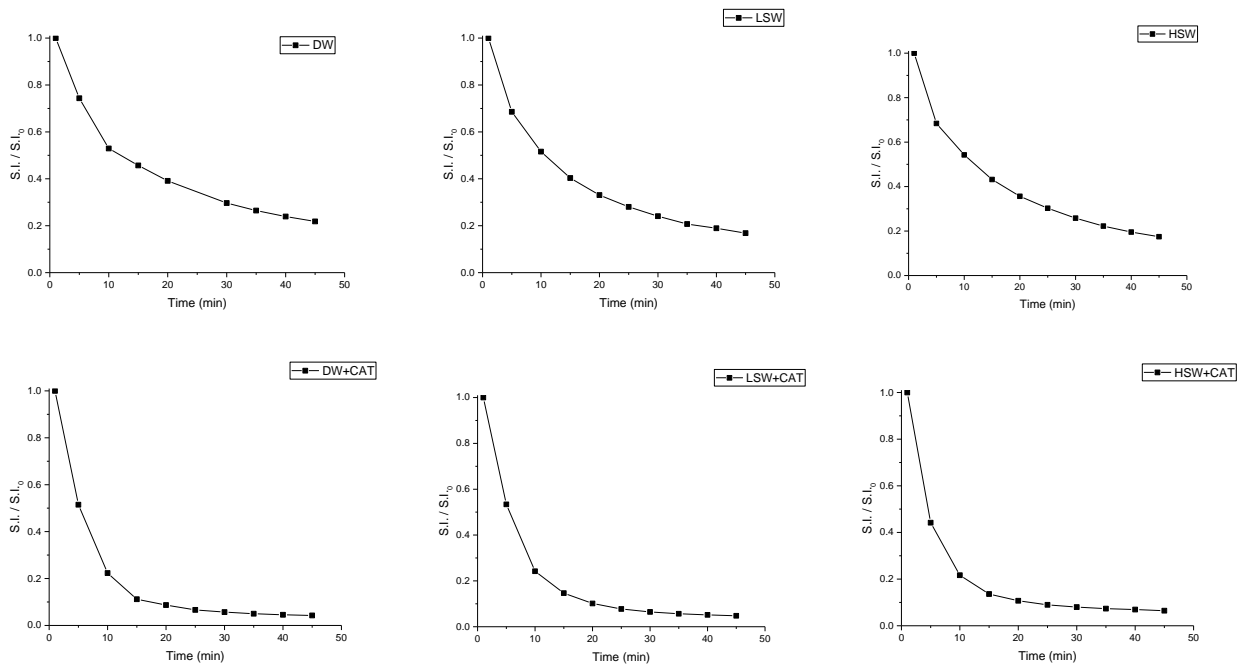
Figure 26. Generation of ·OH at Fenton process in different water matrices and conditions: DW, LSW, HSW, DW+CAT, LSW+CAT and HSW+CAT.

Finally, the generation of hydroxyl radicals was followed over time during the whole process. As can be seen in Figure 26, the presence of chlorides in the medium does not have effect on the ·OH. Nevertheless, the presence of catechol causes the generation of hydroxyl radicals to decrease faster over time. In these cases, the elimination of CECs occurs in the first minutes; therefore, this behaviour does not affect the process, presenting high elimination values after a few minutes.

5. CONCLUSIONS

5.1 General conclusion

Once all the necessary experiments have been carried out to obtain reliable and contrasted results, it can be concluded that humic acid improves the photo-Fenton process when working at pH close to neutral, as in this case working at pH_0 5'0 or pH_0 6'0. Thus, the use of this material can help to improve the photo-Fenton process, reducing the degradation rate times of the CECs present in water.

Within the results obtained and the conditions chosen, the pH close to the circumneutral pH that shows the best results and, therefore, has been studied in greater depth, is pH_0 5'0.

5.2 Specific conclusions

5.2.1 Humic acids substances as a complex agent on the photo-Fenton process at mild pH.

Firstly, the enhancement of the photo-Fenton process due to the use of humic acids as a complex agent of iron was confirmed. This enhancement occurs at pHs near to the circumneutral, in which the velocity of degradation of CECs suffers an improvement, where at 15 minutes they are practically degraded in the presence of HA, being eliminated at 30 minutes in their absence.

5.2.2 pH value closest to the natural one in which the process can be applied efficiently.

Regarding the study of the pH value closest to the natural pH of the water, it was observed that working at pH_0 5'0 presents better results for degradation of CECs than working at pH_0 6'0. This is due to the fact that the optimum pH value of the photo-Fenton process is 2'8; therefore, at a more acidic pH, the process works better. This effect can be observed both in the absence and presence of HA in the medium so that the process works better at pH_0 5'0.

5.2.3 Different sources of humic acids (homogeneous and heterogeneous)

In the case of the study of the heterogeneous process using magnetite nanoparticles coated with humic acid, its use was discarded due to the null or very low performance of the process. This was due to the fact that the iron is not able to dissolve in the medium due to the selected pH ranges, as the solubility of iron(II) and (III) in these circumstances is very low.

5.2.4 Effect of phosphates used commonly as buffers at photo-Fenton processes

As for the study of the effect of phosphates normally used as buffers for Fenton processes, it was corroborated that they have drastic negative effects on the process. Even at very low concentrations, as was the case, 0.16 mM, the process showed a very large reduction in the degradation rate of CECs, being practically eliminated after 10 minutes without the presence of phosphates and between 60 and 120 minutes if they are present in the medium.

This is due to the formation of ferric phosphate, which is highly insoluble. Thus, the iron precipitates rapidly, leaving the medium without dissolved Fe(II) and Fe(III) capable of carrying out the Fenton reaction.

5.2.5 Effect of chlorides on the process and effect of HA

In the case of the study of the effect of chlorides on the process and whether HA is able to enhance the process in their presence, they showed a different behaviour depending on the concentrations of NaCl added. When working with low concentrations of chlorides, in the LSW medium, the process suffered an improvement compared to when it was carried out in DW. This is due to the fact that the presence of chlorides displaces the maximum dissolution of $Fe(OH)^{2+}$ towards higher pH values, therefore, when the process is carried out at pH_0 5, this displacement causes the iron to be more available in the medium, leading to an improvement in the process.

However, if the amount of iron was very high, as in the HSW case study, the process reduced the rate of CEC removal significantly. In this case, what happens is that the high amount of NaCl in the solution makes the interaction between hydroxyl radicals and CECs less probable, as it is more difficult for them to come into contact.

On the other hand, thanks to the use of HA as an iron complexing agent, the process was improved in both cases, following the same order of CEC removal rate as in the processes without the presence of HA: LSW > DW > HSW. However, the presence of HA in the HSW medium does not achieve higher degradation values than in the case of the DW process without HA, which is the reference for the photo-Fenton process.

5.2.6   Use of the electron paramagnetic resonance technique.

Finally, in the case to corroborate the results obtained with the use of the electron paramagnetic resonance technique, the experiments of the production of ·OH presented results that corresponded with the rate of CECs elimination. In these cases, the production of hydroxyl radicals followed the next order depending on the aqueous medium: LSW>DW>HSW, although the difference between them was small.

On the other hand, with the presence of a complexing agent in the medium, the production of hydroxyl radicals increased by about 75% in all cases, following the same order. Thus, it was possible to corroborate how the interaction between complexing agents and iron causes a greater amount of iron to remain active in the medium, thus interacting with H_2O_2 and achieving a higher production of hydroxyl radicals.

5.3 Future research interest

In order to follow up on the work done and implement new options, the main steps to follow would be:

- Study of the process for application in real seawater.
- Carrying out tests in a pilot plant, with a higher volume.
- Study of its possible application at industrial level

5.4 Dissemination of results

The present work will be presented in poster + oral flash format at the 5th Iberoamerican Conference On Advanced Oxidation Technologies (CIPOA), which will be held from 7-11th November 2022 in Cusco, Peru.

Moreover, together with some additional results, an article is being prepared, which will be published in a special issue of 'Catalysis Today'.

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