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Assessment of advanced oxidation processes for the elimination of emerging pollutants in wastewater effluents

Avaliación de procesos de oxidación avanzada para a eliminación de contaminantes emerxentes en efluentes de augas residuais

Evaluación de procesos de oxidación avanzada para la eliminación de contaminantes emergentes en efluentes de aguas residuales

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Index

Abstract/Resumo/Resumen

The increasing industrialization in agriculture supposed an increase in the use of pesticides and other health-threatening substances. Different advanced oxidation processes (direct photolysis, photosensitization, photocatalysis, photo-Fenton and ozonation) for a family of pesticides, the neonicotinoids, will be discussed. Different factors, such as pH, concentration of scavengers, inorganic species, auxiliary oxidants and dissolved organic matter or temperature will be taken in consideration. Methods will be assessed in terms of effectivity, rate and prize. ***Keywords****: Photochemistry, Neonicotinoid, Wastewaters, AOPs, Heterogeneous Photocatalysis, Ozonation, UV Photodegradation.*

A crecente industrialización da agricultura supuxo un incremento no uso de pesticidas e outras substancias perigosas para a saúde do ser humano. Diferentes procesos de oxidación avanzada (fotólise directa, fotosensibilización, fotocatálise, método photo-Fenton e ozonización) foron avaliados para unha familia de pesticidas, os neonicotinoides. Factores como o pH, a concentración de eliminadores de radicais libres, especies inorgánicas e materia orgánica disoluta ou a temperatura foron considerados. A avaliación dos métodos levouse a cabo tendo en conta a súa efectividade, a súa rapidez e o seu prezo. ***Palabras chave***: *Fotoquímica, Neonicotinoide, Augas Residuais, AOPs, Fotocatálise Heteroxénea, Ozonización, Fotodegradación UV*.

La creciente industrialización de la agricultura supuso un incremento en el uso de pesticidas y otras sustancias perjudiciales para la salud del ser humano. Diferentes procesos de oxidación avanzada (fotólisis directa, fotosensibilización, fotocatálisis, método photo-Fenton y ozonización) fueron evaluados para una familia de pesticidas (los neonicotinoides). Factores como el pH, la concentración de eliminadores de radicales libres, especies inorgánicas y materia orgánica o la temperatura fueron considerados. La evaluación de estos métodos se llevó a cabo teniendo en cuenta su efectividad, su rapidez y su precio. ***Palabras clave:*** *Fotoquímica, Neonicotinoide, Aguas Residuales, AOPs, Fotocatálisis Heterogénea, Ozonización, Fotodegradación UV.*

Introduction

The industrial development in the latest years has brought to society not only an increase in the quality of life, but also a rise in the presence of persistent organic pollutants in the environment, especially in aqueous ecosystems. Substances like fungicides, drugs and pesticides tend to accumulate in water, and they pose a serious problem since water consumption implies the incorporation of these harmful substances to the organism.

Nowadays, Wastewater Treatment Stations (EDAR by its acronym in Spanish) are generally not prepared to remove efficiently such toxic species from water. Even though they successfully remove most harmful substances from drinking water, organic persistent micropollutants stay in solution. Possible harmful effects of these substances are neurotoxicity, carcinogenesis or effects on reproduction[1].

This work focuses on a family of persistent organic pollutants: the neonicotinoids (or *neonics*), broadly used in agriculture. These species are neuro-active insecticides and receive their name because they chemically resemble nicotine. Particularly, imidacloprid, clothianidin, acetamiprid, thiacloprid and thiamethoxam are the compounds of main interest, because the European Commission decided to restrict their use in the European Union for its seed treatment purposes. On 27 April 2018, member states of the Union agreed to impose a total ban on neonicotinoid insecticides, with the only exception of closed greenhouse uses. Since only around 5% of the active ingredient of the neonicotinoid is absorbed by plants and the rest disperses in the environment, an efficient degradation of these molecules is crucial[2].
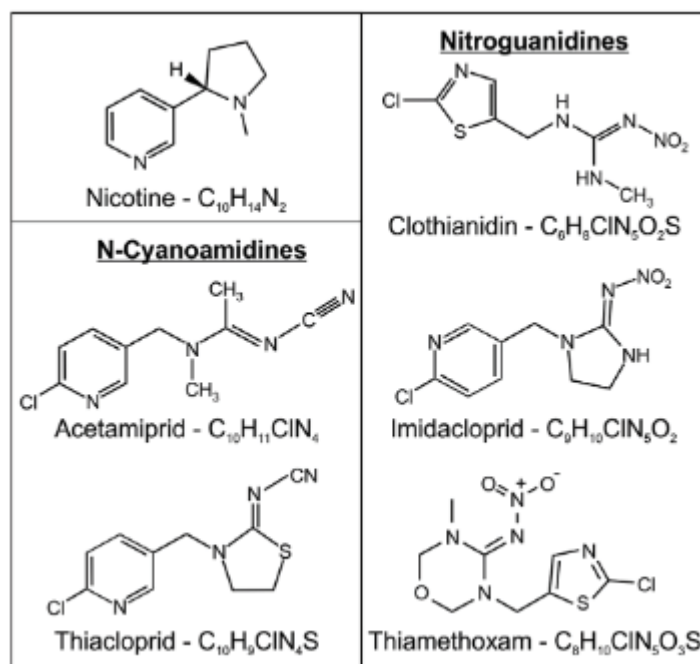
Figure 1: Chemical structure and molecular formula of nicotine and different families of neonicotinoids[3]

Neonicotinoid pesticides are chemical substances used vastly as insecticides, since they exhibit neurotoxic behaviour to insects, by irreversibly binding to their nicotinic acetylcholine receptors[4]. Their toxicity is much greater to insects than mammals due to the much higher presence of these receptors in insects, but the possibility that these compounds may harm mammals (including humans) does exist. For this reason, various methods of depollution of these substances have been studied[5].

In this essay, each technique will be briefly introduced, and its physical-chemical basis explained. The technique will be based in either photochemical or redox phenomena, and the kinetics of the degradation process associated to them will also be presented. Then, a critical revision of each method will be performed, by describing the procedure, results and conclusions of the work of each author. The final objective of this article is to elucidate the best method in terms of efficiency, considering its effectivity to transform the original compounds into innocuous, inorganic compounds such as CO_2, NO_3^-, PO_4^{3-} or SO_4^{2-}. This process is known as *mineralization*.

The physical-chemical methods (Advanced Oxidation Processes) that have special relevance may be classified by their fundament: photochemical or non-photochemical[6].

Examples of photochemical methods are:

- UV light photolysis

- Hydrogen peroxide with UV radiation

- Ozone with UV radiation

- Hydrogen peroxide, ozone and UV radiation

- Photo-Fenton processes

- Heterogeneous catalysis

Examples of non-photochemical methods are:

- Ozonation in alkaline medium

- Ozonation with hydrogen peroxide

- Catalytic ozonation

- Electrochemical/electrocatalytic oxidation
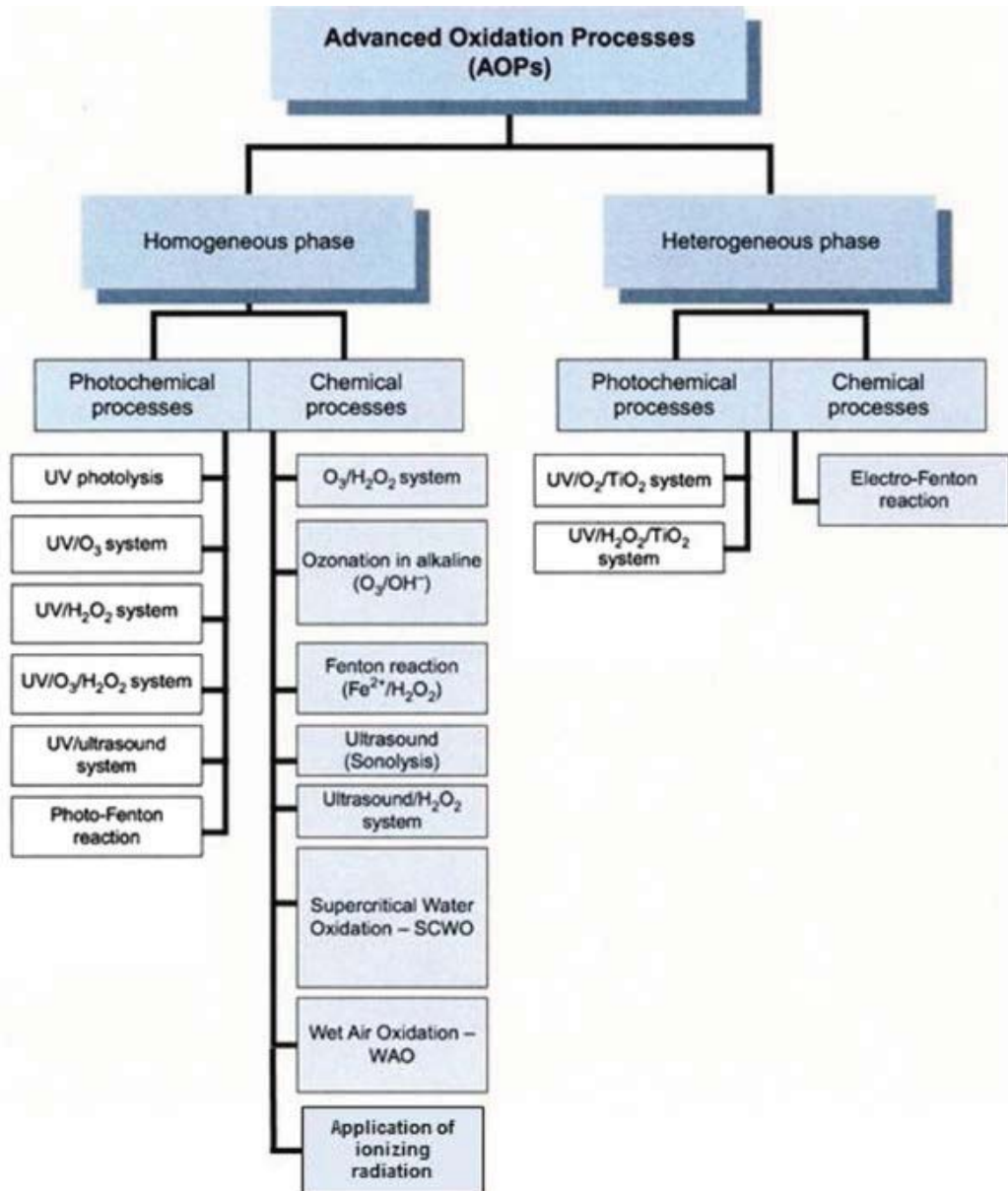
- Radiolysis

- Ultrasounds

Figure 2: Classification scheme of AOPs[1]

Objectives

The objective of this essay is to carry out a critical revision of the literature in what regards advanced oxidation processes, in order to summarize, compare and judge their results,

conclusions and validity of their methods. The influence of different parameters, such as the intensity and wavelength of the radiation, temperature, pH, presence of organic and inorganic species in solution, concentration of oxidant reagents, catalysts and so on will be discussed.

The main goal of this work is to try to understand which method of degradation of neonicotinoid species in solution would have better results in terms of efficiency and effectivity. In order to do it, the criteria taken into account will be the efficiency of the method, the time needed to complete the degradation (at least to a certain percentage), the costs of the method or the complexity of the instrumentation needed to perform the experiment and to check the validity of their results.

Regulations on neonicotinoids, imposed by the European Union, are relatively recent (a partial ban was imposed in 2015, and more strict regulations came into force in 2018[8]), so the bibliographical research will be carried out limiting the date of publication of the different papers since 2015 to the present to review the most recent degradation methods, developed since the start of the ban.

Background

Since the beginning of History, water quality has been a subject of major importance. Life expectancy of Humanity has greatly increased since water potabilization was extended in society; in fact, the possibility of disposing of good-quality water is one of the most important factors improving human life expectancy, comparable to the discovery of vaccination.

The initial objective of water depuration was the removal of harmful components which were in relative high proportions, such as dirt, and eliminate the potentially dangerous microbial species. The increasing development in the pesticide and drug industries supposed a change in the tendency: new substances emitted by industries end up in water and consumed by humans. The capacity to eliminate these chemicals highly depends in the new analytical and physicochemical techniques (the former to detect them and their derivates and the latter to degrade them), since their concentration in water usually belongs in the ppm or ppb range (mg/L or μg/L).

Most of these methods, named *Advanced Oxidation Processes* (AOPs), are relatively new. The term was coined by Glaze et al. in 1987[9] and is referred to the generation of hydroxyl radicals (HO•) in aqueous solution, which are capable to oxidize harmful substances (due to its high value of reduction potential). Even though methods being able to generate this species were already known in the XIX century (treatment with reagents such as hydrogen peroxide or sodium hypochlorite), AOPs seem to be the future reference methods due to their efficiency in the degradation of organic micropollutants.

Other academic work has been carried out before this critical review, with the common objective of describing, summarizing and comparing the different methods and techniques. Burrows et al.[10] reviewed the reaction pathways and mechanisms of photodegradation of different pesticides. This work shares a common structure with the paper mentioned before: a brief description of the technique, and the critical review of different publications considering different experimental factors and conditions. However, it is not the goal of the study to elucidate reaction mechanisms which explain the oxidation process.

Authors reached the conclusion that (at the publication date of the paper), UV light still is the most efficient alternative in order to quantitatively degrade the persistent pollutants of interest, despite its high prize. Photosensitized degradation is a process that may have interesting applications in the degradation of organic matter as well, but sometimes the photosensitizers (auxiliary molecules which transfer energy in their excited state to the

pollutant, as explained later) may be even more toxic than the molecule of interest. Processes based in the generation of radicals may also be useful in the degradation of organic matter, but a major drawback is a possible increase in the toxicity of the generated products. Authors also claimed that, even though the identification of possible products has been widely discussed by different analytical methods, not enough information concerning mechanistic studies was available yet.

Trojanowicz[11] studied the effect of ionizing radiation on waters and wastewaters. First, a description of the physicochemical techniques employed in the oxidation of persistent organic pollutants in water, and then a review of published literature was carried out, according to the chemical nature of each substance (dioxins and furans, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and perfluorinated compounds).

The author conclude that ionizing radiation methods seem to be effective in the degradation of pesticides. It is crucial for the effectivity of the method that the sample preparing is as simple as possible, since multi-step sample preparation are a source of generation of residues. Finally, the author affirms that these state-of-the-art techniques are not systematically employed yet, even though they are effective.

Materials and Methods

The initial purpose of this work was to evaluate the effectivity of several depollution methods (UV photolysis, Adsorption over a catalyst, TiO_2 photocatalysis…) for the removal of a neonicotinoid (imidacloprid) under several experimental conditions, controlling diverse parameters: temperature, pH, saline concentration… The declaration of the state of alarm by the Spanish Government due to the CoViD-19 pandemic made it impossible to access the laboratory and, thus, to carry out any experimental work.

Materials needed to perform this kind of experiment would be the reagents themselves, a source of UVA-Vis radiation, and different instruments (spectrophotometer, HPLC chromatographer…) used to monitor the reaction.

The radiation source (near-UV light was needed to perform some of the intended experiments) would be a Heraeus TQ 150 medium-pressure Hg-vapor lamp, with intense emission lines at excitation = 254, 313, 366, 405, 436, 546 and 578 nm, located axially in the reactor inside a quartz immersion tube. The UV lines at excitation < 366 nm were filtered out using a DURAN 50® glass jacket filled with water, limiting the irradiation to near UV–visible (NUV–Vis).

Both imidacloprid and the TiO_2 catalyst could be purchased from a commercial distributor. An interesting experiment could be the application of XR-D (X-Ray Powder Diffraction) on modified TiO_2 sample (by doping, impregnation), to elucidate its crystalline structure. Commercial TiO_2 has a defined structure (anatase/rutile in an approximate 3:1 ratio, with some amorphous phase), so a way of proving the quality of the catalyst could be the application of this technique. X-Ray fluorescence would be also a technique of choice to study the surface modifications, as well as scanning and transmission electron microscopies (SEM and TEM). To study reaction products, HPLC/MS is the technique of choice.

In order to measure the pH of the solutions of interest, any pHmeter based on a glass electrode could be employed.

The following of the oxidation reaction may be performed by employing a UV-Vis spectrophotometer (since the absorption spectrum may vary under transformation of a species in another). The model employed in the laboratory is the a JASCO V-560 UV-Vis spectrophotometer.

A HPLC instrument could also be necessary to perform the tracing of the reaction. In the laboratory, a Thermo Fisher LC instrument, equipped with a multi-channel pump and a L-2450 diode array detector, is used.

A Total Organic Carbon (TOC) analyser could also be useful to measure the initial and final concentration of organic carbon in solution. The instrument employed in the laboratory is a Shimadzu TOC-5000 analyser equipped with a non-dispersive infrared gas detector (NDIR) and ASI 5000 A Shimadzu autosampler.

Literature Sources and reviewing methodology

Due to the unfortunate circumstances in which this work has been carried out, no presential laboratory activity is shown. In the moment in which the state of alarm was declared, measurements of the UV-Vis spectrum of Imidacloprid in water were performed, along with the UV-Vis evaluation of the hydrolysis reaction of this neonicotinoid (by continuum measurement in the maximum of absorbance of a cell containing an aqueous solution of imidacloprid).

The search of information has been carried out by using several databases which may be accessed from University of A Coruña, like Web of Science (*WoS*) and Scopus. An open-access web search engine (Google Scholar) has also provided the student with some sources of information. Finally, some resources have been provided by the tutor and other members of the React! Group.

The information search was carried out using keywords: first, the name of the technique/AOP (photolysis, photocatalysis, photo-Fenton…) and then, the name of the substance in question (neonicotinoid, acetamiprid, imidacloprid…). The results were

refined by decreasing number of citations (selecting first the papers with a higher number of citations) and then inspected.

The reference manager Mendeley has also been used for bibliographic organization purposes.

A total of 14 articles reviewed in this work were published from 2015 to the present. Since the EU regulations were firstly implanted in 2015, and tightened in 2018, it is reasonable to set a 5 years range for the critical review. However, other publications outside of this time range have been used for different purposes, like the discussion of the previous work carried out in this field or the explanation of the physical fundament of the techniques in question.

Workplan and Schedule

The workplan and schedule of this final degree dissertation have been obviously conditioned by the exceptional circumstances related to the CoViD-19. The initial idea was to spend a brief period (3 weeks) of bibliography search, followed by a second period of experimental work in the laboratory. The discussion of the obtained experimental data and writing of the memoir would be the culmination of the work. The shutdown decreed by the Spanish Government implied a complete change of plans.

Around the third week of April, the tutors and the student discussed the possibility of changing the work into a critical revision, deciding to eliminate the contribution of the experimental work of the essay. Since that moment, an exhaustive search of bibliography and the starting of the draft writing have been carried out, with periodical revisions of the written work by the tutor.

The months of May, June and July were devoted to writing up the final version of this bachelor thesis degree.

Critical Review

In this chapter, the results of the critical review will be discussed. The procedure of discussion will involve an explanation of the physical-chemical fundament of each technique, followed by a critical comment on the results obtained by each group.

Direct photodegradation

UV light photolysis is a process in which a source of radiation is set in contact with the sample (in aqueous solution), in order to favour its decomposition. Ideally, the sample should be let in contact with sunlight. This approach has not great relevance, since even though this kind of pesticides absorb UV radiation, the percentage of ultraviolet solar light that arrives to the atmosphere is rather low. In fact, pesticides are generally designed to be stable towards sunlight. The alternative, though, is sometimes difficult to apply in the large scale, since the generation of UV radiation (by Hg or D_2 lamps, mostly) is rather expensive.

The process of direct photodegradation can be described in a series of steps. First, the molecule will absorb a photon of energy **hv** and will be promoted to the excited state. The excited state, which is unstable, may undergo heterolysis, homolysis or photoionization. Other processes, such as emission of energy in the form of heat, are also possible. The photolysis process is described below[12]:

$$PX + h\nu \rightarrow PX^*$$

Scheme 1: absorption of radiation by a molecule.

$$PX^* \rightarrow P^\bullet + X^\bullet$$
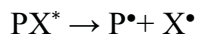
Scheme 2: homolysis of a molecule from its excited state.

$$P^- + X^+ \leftarrow PX^* \rightarrow P^+ + X^-$$

Scheme 3: possible heterolysis processes of a molecule from its excited state.

$$PX^* \rightarrow (PX)^{\bullet+} + e^-_{aq}$$

Scheme 4: possible photoionization of a molecule from its excited state.

The identification of the products generated after the process may be performed employing High-Performance Liquid Chromatography, by comparison of the retention times of each of the peaks with available standards. In order to identify the kinetics of the process, an option is to employ UV-Vis spectroscopy. The full spectrum of the molecule may be measured over time (in lapses of a certain quantity of time) or, in order to speed up the process, only the maxima of the spectrum can be recorded.

Acero et al.[13] studied the photodegradation of neonicotinoids by monochromatic UV radiation (254nm). One experiment involved a $500cm^3$ cylindrical glass reactor at constant temperature (20^oC) and magnetically stirred and filled with $1\mu M$ solutions of one neonicotinoid buffered with phosphoric acid/phosphate (10mM). Also, other experiments considered the presence of inorganic anions (bicarbonate, nitrate, nitrite and chloride), in order to study the effect of those species in the degradation process. The concentration of each neonicotinoid was determined by HPLC measurements. TOC was determined employing a total organic carbon analyser and pH measurements were carried out with a multiparameter instrument.

The degradation rate of each neonicotinoid is calculated after the experiment. The difference in the degradation rate of each pesticide may be attributed to their different structures; the nitroguanidine functional group present in thiamethoxam and imidacloprid is quite prone to photolysis. In the other hand, cyanoimine functional groups, like the ones in thiacloprid and acetamiprid, are stable to light irradiation.

The effect of pH in the degradation experiments is also taken into account. It seemed that quite similar yields for the degradation are obtained regardless of the pH value. Less reactive compounds (thiacloprid and acetamiprid) exhibited slightly higher tendency to degradation at pH 5.

Also, experiments were carried out in presence of tert-butyl alcohol (a typical scavenger of hydroxyl radicals). The nature of this compound implies that the major process of photodegradation is direct photolysis. The values of $X_{t=2\ min}$ at pH =7 are rather similar in presence and absence of t-BuOH, implying that the photodegradation by alternative pathways to direct photolysis may be negligible. At pH = 5, there exists a small contribution to this pathway, but it must be considered that the rate of the process for acetamiprid is rather low.

The effect of inorganic species on the photodegradation process (since they are present at significative concentration in wastewaters) is evaluated as well. These anionic compounds may affect the photodegradation rate, since they could generate radical species, favouring the process of oxidation, or react with hydroxyl radicals and thus inhibiting the photochemical degradation. Anions of interest are bicarbonate, nitrate, nitrite and chloride. These anions, apparently, have nearly no effect on the photodegradation yields for thiamethoxam, imidacloprid, clothianidin and thiacloprid; only a slight decrease in the rate of degradation of thiacloprid is noticed. In conclusion, the impact of those anions in direct UV photolysis may be negligible. Nevertheless, the yield of photodegradation for acetamiprid is decreased by the presence of these anions, since they act as scavengers of •OH radicals.

Todey et al.[14] proposed a different approach to the problem. The source of radiation was a solar simulator, equipped with a Xe-arc lamp (290nm) and natural sunlight. Solutions were prepared in ultrapure water and water from Mississippi River, from an aqueous stock solution. Further experiments were also performed in order to determine the influence of nitrate anion in the photolysis process. Light absorbance of each pesticide was measured by UV-Vis spectrophotometry (200-800nm). The identification of the reaction products was carried out by UHPLC-MS/MS.

The results show that quantum yields in for imidacloprid, thiamethoxam and clothianidin are larger in Milli-Q water than in Mississippi River water. Acetamiprid samples, exposed to the radiation in the solar simulator, gave an estimated half-life greater than 100h, much longer than the values reported in literature. Moreover, the exposure of this compound to solar radiation for more than 1 month did not produce any degradation process, so it can be concluded that solar photodegradation of acetamiprid does not happen.

This study did not consider the effect of pH or other anions than nitrate in the direct photolysis of neonicotinoids. Also, the temperature was not monitored during the process.

Lu et al.[15] employed a Photochemical Reactor, with 16 medium-pressure Hg lamps with a range of spectral emission from 250 to 400nm. Irradiation vessels, filtering radiation with $\lambda < 290$ nm, were employed: Pyrex tubes of 50mL. P-nitroanisole/pyridine and p-nitroacetophenone/pyridine actinometer systems were employed to monitor photon flux in the photoreactor. In their experiments, acetamiprid, thiacloprid and thiamethoxam neonicotinoids were the species of interest.

Their experiments showed that the photolysis of neonicotinoids followed a pseudo-first order kinetics, and no loss of species was observed in the dark, concluding that no hydrolysis of the neonicotinoids takes place. In this experiment, the half-lives of the species are 12±0.4 min, 12±1.1 min, 22±1.3 min, 26±1.0h and 42±1.6h for imidacloprid, clothianidin, thiamethoxam, acetamiprid and thiacloprid. This result may be surprising,

since the results obtained by Acero et al. supposed a half-life order of thiamethoxam < clothianidin < imidacloprid < thiacloprid < acetamiprid. These discordance in the photodegradation rates may be explained by a main factor, which is the wavelength of the applied radiation. The alternative explanation (that the degradation of the pesticide may be occurring via other processes) is, in absence of a photocatalyst or a photoreactive species, negligible.

Unlike Acero et al.[13], Lu et al[15]. do not consider factors such as temperature, pH range, or presence of hydroxyl scavenging species or ionic compounds in solution.

The impact of organic matter and Cl^- in the photodegradation of acetamiprid is object of study by Pinto et al.[10] Water samples from a coastal lagoon and two rivers that provide that lagoon with water were taken and filtered through a 0,7μm glass microfiber filter. An UV-Vis spectrophotometer was employed to measure absorption spectra of the samples, and identification of the products was achieved by using HPLC with DAD determination. The radiation source for the experiment was a mercury lamp, emitting in the 200-400 nm range and kept to ambient temperature (20 ± 2 ºC) with a cooling jacket containing tap water.

First, degradation of acetamiprid in model water matrices (standardized solutions contained determined concentrations of dissolved organic matter, dissolved salts and pH) was studied. The solutions considered only chloride anions (and their sodium counterions) as accountable for the salinity of the solution, since sodium chloride is the major ionic compound in marine waters. The degradation followed pseudo-first order kinetics (only the concentration of acetamiprid depended on the reaction rate) and was almost fully related to photolysis (since samples not submitted to radiation only lost less than 2% of initial concentration of acetamiprid).

Experimental results show that pH (in the 5-9 range) does not seem to have a strong impact in the degradation of the pesticide degradation. However, the concentration of halide ions (Cl^-, Br^- and I^-) appears to play an important role in the kinetics of the process.

The constant of the process increases with the increasing concentration of Cl^-. When adding sodium bromide or sodium iodide, the constants are lower than when adding sodium chloride. This effect could be explained by the formation of the corresponding dihalide radical anions ($X_2^{-\bullet}$), in a three-step process that is proposed below[16]:

$$2X^- + h\nu \rightarrow X_2 + 2e^-$$
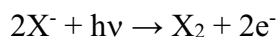
Reaction 1: photochemical oxidation of the halide.

$$X_2 + h\nu \rightarrow 2X^\bullet$$
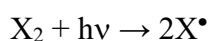
Reaction 2: homolysis of the halide.

$$X^\bullet + X_2 \rightarrow X_2^{-\bullet}$$
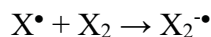
Reaction 3: generation of the dihalide radical anion.

$Cl_2^{-\bullet}$ radical anions are less stable than $Br_2^{-\bullet}$ and $I_2^{-\bullet}$ anions, as inferred by measurement of their standard oxidation potentials to yield the corresponding halide (+2,126 V for $Cl_2^{-\bullet}$, +1,63V for $Br_2^{-\bullet}$ and +1,03V for $I_2^{-\bullet}$). An additional effect explains the decrease in the reactivity for iodine anionic radical: the formation of triiodide anions (I_3^-) which do not degrade organic matter.

The addition of a $HO^\bullet$ radical scavenger (isopropanol), in a concentration of 35g/L, resulted in a decrease of the kinetic degradation constant. Since this species does not react with the anionic halogen radicals discussed before, the decrease in the photolytic activity could be explained by a drop in the concentration of $HO^\bullet$ radicals in the medium, which are involved in the degradation of the neonicotinoid. Furthermore, this substance is UV-active (presents a maximum of absorbance at 264nm that could be attributed to impurities such as aromatic compounds); the absorbance of UV radiation by isopropanol impedes the interaction of light with the pollutant and inhibits direct photolysis processes.

Substituting NaCl by an equivalent inert salt (Na_2SO_4) in the same extent (maintaining the ionic strength constant) reduced the degradation rate, confirming than radical anion halogens play a role in the oxidation process. Moreover, the rate is increased in solutions containing Na_2SO_4 with respect to unbuffered solutions (only containing the pollutant in Milli-Q water, in absence of salt), suggesting that ionic strength is a factor to take into account during the degradation mechanism (for example, by stabilization of ionic intermediates by ions in solution).

Finally, the effect of dissolved organic matter (DOM) is discussed. Humic acid from a commercial distributor and samples from Suwanne river containing humic and fulvic acids, respectively. Proposed structures for these substances (with non-strictly defined chemical structure and formulas) are detailed in *Figure 3* below:

(a) **Humic Acid** (Stevenson 1982)

(b) **Fulvic Acid** (Buffle 1977)
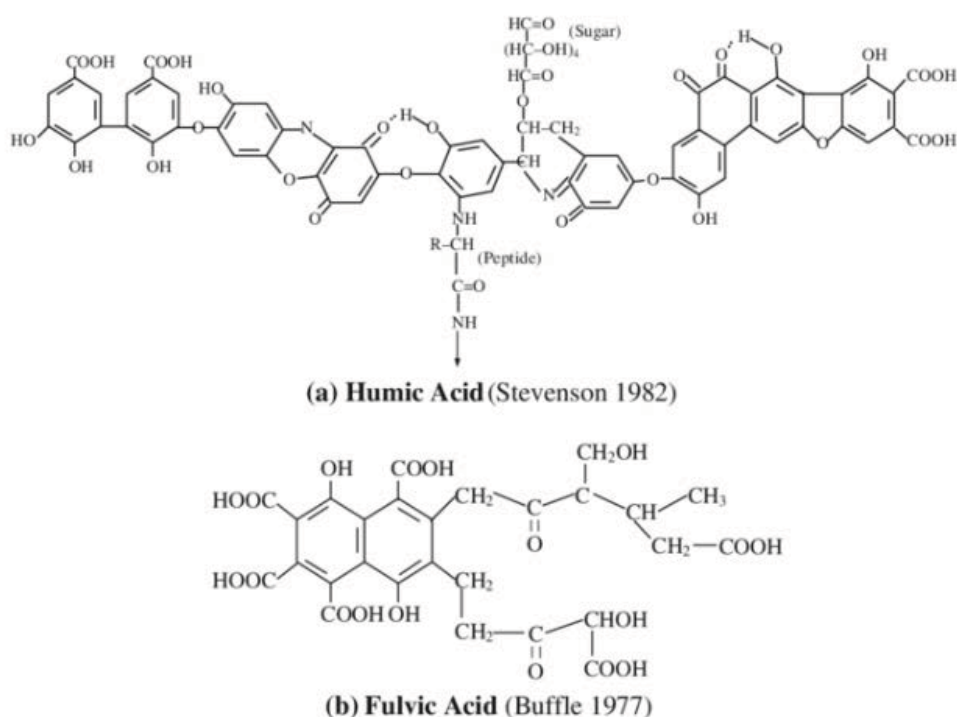
Figure 3: Proposed structures for humic and fulvic acids [17]

Results show that the increase in concentration of commercial humic acid decreased the rate of the degradation process. For experiments performed with organic matter in river samples, the decrease in the degradation rate drastically falls. This fall in the activity may

be explained by the interaction of organic matter with radiation: solvated electrons, singlet oxygen, superoxide anion, hydroxyl radical… are reactive species that are generated in solution when DOM is irradiated with UV light. However, after the reaction of these species with the pollutant, it reacts with DOM again, resulting in the regeneration of the molecule of the neonicotinoid. The reaction scheme is proposed in *Figure 4*:
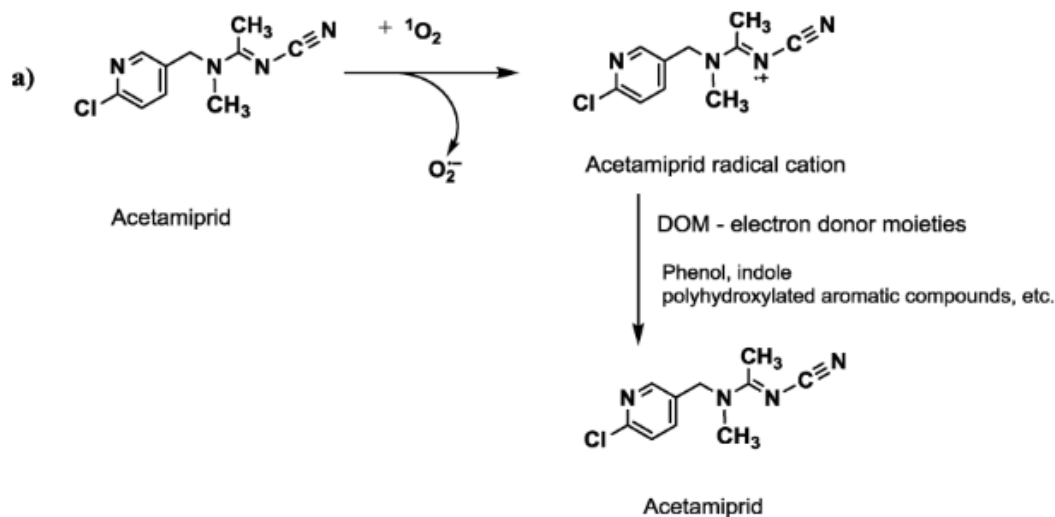

Figure 4: regeneration of acetamiprid after reaction with singlet oxygen. [10]

DOM acts as electron acceptors, so fulvic acid, as a more aromatic substance, has a greater capacity of accepting negative charge, and therefore can deactivate radical acetamiprid ions, as results show.

Authors do not consider temperature influences in the degradation process. Mechanistic studies are also not carried out.

Photosensitized photodegradation

Other approach to achieve the degradation of the pesticides is the photosensitized photodegradation. This method involves an auxiliary species (the photosensitizer), which interacts with the radiation and promotes to an excited state. The photosensitizer then may transfer energy to the substance of interest, which may undergo processes described in Schemes 2, 3 and 4[18].

The interest of this approach lies in the possibility to employ longer wavelengths in the excitation of the photosensitizers than the ones required to directly photolyze the molecule of interest. Longer wavelengths suppose lower values of radiation energy, and less energetic sources of radiation tend to be cheaper than low-wavelength lamps.

There are many examples of photosensitizers, as an incommensurable number of molecules interact with radiation.

Yin et al.[19] studied the oxidation of some neonicotinoids in tap water (specifically imidacloprid and thiacloprid) by photosensitized degradation, employing molecular chlorine as a photosensitizer. Their study focused on the role of molecular chlorine (and its derivatives), and other parameters such as the effect of pH and other species in the degradation process.

Their results showed that the introduction of chlorine boosted the rate of degradation for both species. Direct UV photolysis of these neonicotinoids follow pseudo-first order kinetics (with a rate value of $2,88 \times 10^{-4}$ s^{-1} and $1,25 \times 10^{-4}$ s^{-1} for IMD and THIA), but 270μM initial concentration of chlorine increased the rates to $5,74 \times 10^{-4}$ s^{-1} and $2,54 \times 10^{-4}$ s^{-1}.

The effect of a hydroxyl scavenger (tert-butyl alcohol) was also studied. The rates of reaction for the degradation were reduced, but complete inhibition was not observed. The

study of consumption of Cl• radicals by the scavenger was not completely carried out due to the lack of data (no reaction rate of Cl• with the neonicotinoid data is available).

The influence of pH in the process was discussed as well. For direct photolysis of the neonicotinoids, no influence of this parameter in the rate of degradation was observed. For chlorine degradation processes, a decrease in pH favoured the degradation of thiacloprid. The authors proposed a kinetic stabilization of HClO at low pH, which favoured the chlorination of the pesticide, as a possible explanation to that experimental result.

In this study, the effect of temperature in the degradation was not considered, not even mentioned.

Abramović et al.[20] focused only on one neonicotinoid (thiacloprid). They used a Hg high pressure lamp with emission bands at $\lambda > 290nm$, having the emission maximum at 366nm. Their experiment supposed a failure, since the absorption spectrum of the compound did not overlap with the emission spectrum of the lamp, resulting in no absorbance of radiation by the substance. Consequently, no degradation was observed. The experiment was carried out at natural pH (pH=6), and 240 minutes after the start of the irradiation no degradation was observed.

Concentration of hydrogen peroxide is then considered. A positive correlation between the concentration of H_2O_2 and the efficiency of degradation appears to exist. A possible explanation could be the generation of hydroxyl radicals by homolysis of the O-O bond in hydrogen peroxide, very oxidant species. As the initial concentration of H_2O_2 increases, more hydroxyl radicals will be available to oxidize organic matter, resulting in a greater oxidation rate. An optimal concentration of hydrogen peroxide (220mM) is obtained.

The influence of pH of the solution is also studied. The yield of the degradation is evaluated in a pH range of 2.9 and 9. Results showed that the process is more efficient at more acidic pH. The explanation to this experimental fact may be found in a competing process involving hydroperoxyl radical and hydrogen peroxide:

$$HO_2^- + HO^\bullet \rightarrow HO_2^\bullet + HO^-$$
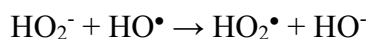
Reaction 4: scavenging of hydroxyl radicals by hydroperoxide anion.

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^-$$
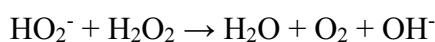
Reaction 5: decomposition of H_2O_2 by reaction with hydroperoxide anion.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$
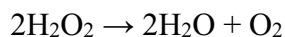
Reaction 6: spontaneous decomposition of hydrogen peroxide.

Hydroperoxyl anion scavenges hydroxyl radicals, in fact, the scavenging reaction is 100 times faster than the H_2O_2 decomposition reaction. At lower pH, the reaction is more favoured than at alkaline pH (by disappearing of HO^- ions as they react with hydronium cations). However, the spontaneous self-decomposition of H_2O_2 is a much more favoured process under basic conditions. Experimental results showed that the ideal pH value for this experiment is 2.8, which shows that the spontaneous decomposition of hydrogen peroxide is a more important factor than the scavenging of hydroxyl radicals by hydroperoxide anion.

The photosensitized degradation process is then evaluated in natural waters. The matrix in ultrapure water is rather different that the one in natural waters, since there are inorganic species, natural organic matter and other molecules in the latter that could negatively impact the degradation process. To evaluate this process, two samples (natural and distilled water) were treated with hydrogen peroxide (5mM and 45mM, respectively), and the degradation efficiency was evaluated.

Results showed that there were practically no differences between the degradation rate of thiacloprid in distilled or natural water. It appears that UV-H_2O_2 photosensitized degradation is a method that could be applied independently of the matrix in question, if it were natural water.

Authors conclude that, even though the degradation of imidacloprid can be obtained in a rather efficient way, total mineralization of the sample is not achieved, and after long periods of irradiation (35h), a relatively high percentage of organic carbon remains unmineralized (17%). The method necessarily requires the presence of both elements (UV radiation and hydrogen peroxide) to be successful, since no mineralization is observed when they operate alone.

Photocatalytic degradation

Even though the application of UV radiation is an effective process, it is also an expensive method of degradation of persistent pollutants. Alternative approaches, involving cheaper sources of radiations (ideally, sunlight), aim to complete the degradation of organic matter using different catalysts, generally, of semiconductor nature.

Semiconductors are materials which possess electrical conductivity by electron mobility between two energy levels (gaps) separated by an energy barrier or gap (E_g). The first band (the valence band) is completely full of electrons, and the second band (the conduction band) is completely empty, as shown in *Figure 5:*
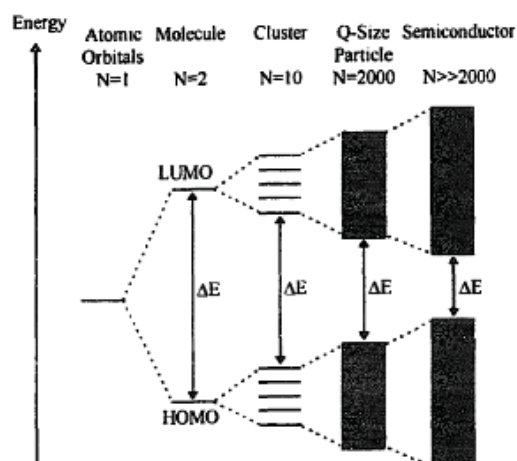
Figure 5: Electronic structure of a semiconductor[21]

This energy barrier is sufficiently low (normally not higher than 4eV) to satisfy the resonance condition with radiations of relative low wavelengths (for example, sunlight). In addition, this kind of catalysts must have adsorption properties; their surface interaction with the pollutant is key to its efficient degradation.

The photocatalytic degradation starts with the surface adsorption of the pollutant over the catalyst, a "dark" process in which no radiation whatsoever is involved. At the same time, radiation is applied. If the energy of the radiation source is equal or greater than E_g, an electron from the valence band is promoted to the conductivity band, generating a "hole" (h^+, with oxidizing properties) and an "electron" (e^-, with reducing properties). This polarization is, by nature, unstable, resulting in the nearly immediate neutralization of the e^-/h^+ pair and energy liberation in the form of heat. However, some pairs reach the surface of the catalyst and trigger redox reactions. Holes, as oxidants, react with electron-donors (-OH groups, water…). They generate hydroxyl radicals.
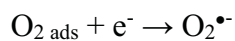
$$h^+ + H_2O_{ads} \rightarrow H_2O^{\bullet +} + HO^\bullet$$
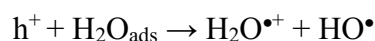
Reaction 7: generation of hydroxyl radicals by reaction of water with holes.

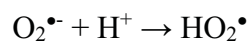$$h^+ + OH^-_{ads} \rightarrow HO^\bullet$$
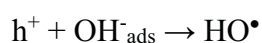
Reaction 8: generation of hydroxyl radicals by reaction of hydroxide anions with holes.

Electrons, which are reducers, may react with acceptor species such as molecular oxygen. Superoxide anion, a reactive oxygen species (ROS) is generated.

$$O_{2\ ads} + e^- \rightarrow O_2^{\bullet-}$$

Reaction 9: reduction of adsorbed oxygen to yield superoxide anion

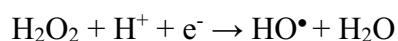$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$$

Reaction 10: generation of hydroperoxyl radical in acidic medium.

Dismutation of superoxide anion and hydroperoxyl radical ($HO_2^{\bullet}$) yields hydrogen peroxide, which is also a source of hydroxyl radicals.

$$O_2^{\bullet-} + HO_2^{\bullet} + H^+ \rightarrow H_2O_2 + O_2$$

Reaction 11: Generation of hydrogen peroxide

$$H_2O_2 + H^+ + e^- \rightarrow HO^{\bullet} + H_2O$$

Reaction 12: Generation of hydroxyl radicals by reduction of hydrogen peroxide

Concluding the process of photocatalysis[22]. The process is summarized in *Figure 6* below.
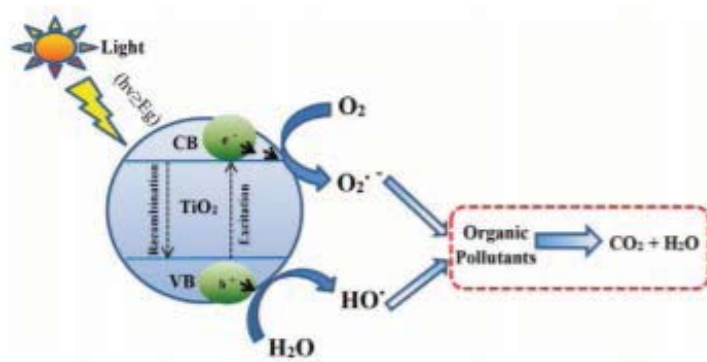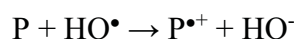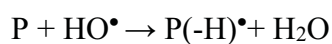
Figure 6: Mechanism of Photocatalysis[23]

HO$^{\bullet}$ radicals are very useful species in the degradation of organic matter. Their high reduction potential makes them powerful oxidants. Once in contact with the adsorbed pollutant (P), several radical reactions may occur[24]:

$$P + HO^{\bullet} \rightarrow P^{\bullet +} + HO^{-}$$

Scheme 5: monoelectronic oxidation of a pollutant by hydroxyl radicals

$$P + HO^{\bullet} \rightarrow P(-H)^{\bullet} + H_2O$$

Scheme 6: hydrogen abstraction reaction by hydroxyl radicals

$$P + HO^{\bullet} \rightarrow (POH)^{\bullet}$$
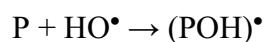
Scheme 7: hydroxyl addition reaction

The efficiency on the oxidation of the organic product depends on the product itself, the catalyst, and the employed radiation. Other parameters such as pH, temperature, scavenger species, ionic strength … may also affect the yield of the degradation.

Garrido et al.[25] studied the degradation of several pesticides, including two neonicotinoids (acetamiprid and thiamethoxam), employing TiO_2 as a photocatalyst. An auxiliary oxidant agent ($Na_2S_2O_8$) was also employed. They used a depuration system, featuring a photoreactor in which the photocatalysis process occurs.

The concentration of both species (the catalyst and the oxidant) was optimized prior to the starting of the photocatalysis. The concentration of reagents at which no increase in the efficiency of the process is observed was determined to be 300mg/L for both substances.

The concentration of each pesticide was determined by HPLC-MS/MS from time to time. The quantity of pesticide when the photoperiod (lapse of time in which the pollutant is exposed to radiation) had concluded depended on the nature of pesticide, but for the neonicotinoids of interest was rather low (39% for acetamiprid and 21% for thiamethoxam). Degradation of these species followed a first-order kinetic model. The reaction rate, in general, was observed to increase as the initial concentration of pesticide increased.

The water sample used in this experiment had a pH = 8,22; the concentration of inorganic species was also determined (Na^+, K^+, $Ca^{2+,}$ Mg^{2+}, Cl^-, NO_3^{3-}, PO_4^{3-} and CO_3^{2-}). Electric conductivity parameter was also controlled. The sample was subjected to a pre-treatment step (phytosanitary treatment).

Berberidou et al.[26] considered the degradation of a single neonicotinoid (thiacloprid) by TiO_2 photocatalysis. Several parameters (initial amount of pesticide and catalyst, pH and existence of electron scavengers) were considered as well. The structure of the catalyst is well-defined, containing anatase and rutile in a ratio 3:1, with some amorphous phase (P25 TiO_2).

They used a photocatalytic reactor (500mL of volume) and considered an initial pH of 5.0±0.1 and a constant temperature of 25±0.1ºC. The maximum absorption of the pesticide over the surface of the catalyst was reached in a lapse of 30 minutes. Some instruments were used to obtain analytical information: an UV-Vis spectrophotometer was employed to relate the absorbance of the sample to the concentration of pesticide, a TOC (Total Organic Carbon) analyser was used to determine the dissolved organic carbon, a Shimadzu system was used to determine the concentration of ionic species, and a LC-ESI/MS was employed to determine the concentration of the generated products after the degradation of the pesticide. Acute toxicity was determined by bioluminescence measurements of the marine bacteria *Vibrio fischeri*[27], while phytotoxicity was determined employing a standard bioassay, based in the evaluation of germination and root growth of different eukaryotic species.

The effect of the concentration of the catalyst is firstly studied. The efficiency of the process increases with the concentration of the catalyst until a certain quantity, the saturation value (0,5 g/L). A further increase in this quantity asymptotically decreases the efficiency of the process (due to different factors, like the decrease in penetration of UV radiation by the presence of suspended particles in solution or the interactions between particles, limiting the active surface).

The effect of the concentration of the neonicotinoid is evaluated. Dark adsorption experiments are carried out, resulting in a pseudo-first order reaction. For these experiments, a concentration of catalyst of 0,5 g/L was employed, and values of k (limiting rate constant at maximum coverage, 1.10 ± 0,23 mg/L min) and K (equilibrium constant for the adsorption process, 0.02 ± 0.003 mg/L) were calculated.

Initial pH is an important factor, since electrostatic interactions between the pollutant and the surface depend on this parameter. The optimization of the pH value may improve the degradation efficiency. The initial degradation rate of the neonicotinoid achieves an optimal value at pH near 9.0.

Electron scavengers are also responsible for the degradation, via generation of reactive oxygen species, of pollutants. The concentration of a scavenger (hydrogen peroxide) is studied. The reaction of this species with solvated electrons or with superoxide ions may generate hydroxyl radicals, which oxidize organic matter.

$$H_2O_2 + e^- \rightarrow HO^- + HO^\bullet$$
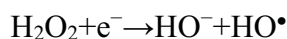
Reaction 13: Generation of hydroxyl radicals by reduction of hydrogen peroxide

$$H_2O_2 + O_2^{\bullet-} \rightarrow HO^\bullet + OH^- + O_2$$
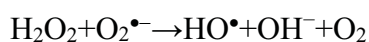
Reaction 14: Generation of hydroxyl radicals by reaction of hydrogen peroxide with superoxide anion.

An optimal concentration of H_2O_2 is necessary to maximize the generation of $HO^\bullet$ radicals, without reacting with catalyst particles, disabling the photocatalysis process. The concentration in question is determined to be 100mg/L.

The effect of temperature in the reaction rate is not discussed. The authors do not specify the presence of a thermostat, or a value of temperature at which experiments are carried out. Also, the presence of inorganic species (ions that are usually in aqueous solution) is not discussed as well.

Authors conclude that the degradation of thiacloprid via photocatalysis, employing TiO_2 as the photocatalyst, is an effective process that could have potential interest in wastewater treatment.

Tabasum et al.[28] discussed the degradation of only one neonicotinoid (acetamiprid) by photocatalysis, employing graphene-oxide-based metal ferrites as catalysts. Their work

consisted in a first step (synthesis and characterization of the catalyst) and a second step (analysis and optimization of the variables affecting the degradation process).

The synthesis and characterization process will not be object of discussion in this work.

For the degradation experiment, a shaker was employed to maintain constant agitation of the sample. A UV chamber was employed as the radiation source (254 nm), and a spectrophotometer was used to evaluate the degradation percentage of the neonicotinoid (employing a radiation of 245 nm, corresponding to the maximum of absorbance of acetamiprid). The calculation of the degradation was carried out taken as reference the untreated neonicotinoid solution.

The effect of pH of solution is firstly studied, in the range of 2-8. Experimental results showed that the degradation was enhanced under acidic pH conditions (pH=3), and the efficiency of the oxidation process decreased as pH increased. A possible explanation to this experimental fact is that the surface of the catalyst becomes protonated at low pH values, promoting the generation of OH^- ions which favour the homolysis of the molecules of the oxidant. When the oxidant decomposes, $OH^\bullet$ radicals are generated, and non-selectively oxidize organic matter, whereas the catalyst surface is deprotonated in alkaline conditions, and such effect does not take place.

Another effect, related to the reactivity of ferrous ions in alkaline medium, must be considered: the reaction of the cations of the catalyst with hydroxyl anions yields a photocatalytically inactive substance, iron (II) hydroxide (Fe $(OH)_2$). This insoluble salt ($K_{ps} = 8,0 *10^{-16}$) forms colloids and sludges impeding the penetration of light, as well as blocking possible active surface sites.

Later, the effect of the concentration of the oxidant is taken into consideration. Hydrogen peroxide is added to the solution in order to enhance the oxidation process, as it promotes the generation of hydroxyl radicals via homolysis. The concentration range of interest is

1,16-58mM H_2O_2. Experimental results showed that the optimal value of concentration of oxidant is in the middle of this range (21.75mM for $MnFe_2O_4$ and 36,25mM for $NiFe_2O_4$).

Low proportions of hydrogen peroxide yield relatively low concentrations of hydroxyl radicals and decrease the efficiency of the process. As the concentration of oxidant rises, the degradation of the pollutant is increased, until the optimal concentration of oxidant. Above this value, the efficiency of the degradation starts to drop again.

This experimental fact is consistent with a two-factor explanation: on the one hand, hydrogen peroxide molecules compete for the adsorption sites of the catalyst with the organic molecules. Higher concentration of oxidant implies that fewer organic molecules will be adsorbed and thus oxidized. On the other hand, at relatively high concentration of H_2O_2, the oxidant reacts with itself yielding peroxyl radicals, which, even though is an oxidant species too, has less capacity to oxidize organic matter.

The effect of the initial catalyst dose in the degradation yield is subsequently studied, in the range of 0-200 mg/L. An optimal value of 100mg/L of catalyst is found. As the concentration of the catalyst increase, a higher number of active sites will be available for adsorption, and more molecules of pesticide will be adsorbed. Moreover, an increase in the number of sites supposes an increase in the hydroxyl radical generation. At concentrations higher than 100 mg/L, particles of the catalyst start to aggregate, provoking a decrease in the number of active sites. Furthermore, light penetration is reduced as the number of suspended particles increase, decreasing the production rate of hydroxyl radicals.

Initial concentration of acetamiprid is now discussed, in the range of 2-16 μg/L. Experimental results show that degradation dramatically decreases as the concentration of pesticide increases, even though at low concentrations (2-8 μg/L), virtually full degradation is obtained. Two factors give an explanation to this data: as the concentration increases, there will be a larger number of molecules in solution, and some of them will

not be adsorbed and thus will not experiment degradation. Moreover, a larger concentration of molecules will suppose a higher UV absorption, resulting in fewer photons available for the photocatalytic process.

The irradiation time with monochromatic UV light (λ=254 nm) is also object of study. Results showed that the degradation of the pesticide proceeds majorly during the first hour of the process. Further increases of time asymptotically increase the degradation to a certain value of equilibrium, close to 100% degradation.

Finally, a study of the reusability of the catalyst over time was performed. After treatment of acetamiprid under optimal conditions (the ones described above), the catalyst was removed from the solution by the application of a magnetic field, treated with ultra-pure water and dried at 60ºC in the oven. After 5 photocatalytic cycles, the efficiency of the catalyst only had decreased in a 5-10%, being the catalyst suitable for its recycling. A study of iron leaching (transfer of iron ions from the catalyst to the solution) was also carried out by atomic absorption spectroscopy, yielding values much lower than the EU regulations (2,0 mg/L). Drinking water which was treated under this method would be, in principle, safe for consumption.

The publication concludes with a comparison of the effectivity of different methods of acetamiprid removal, as it can be shown in *Figure 7*:
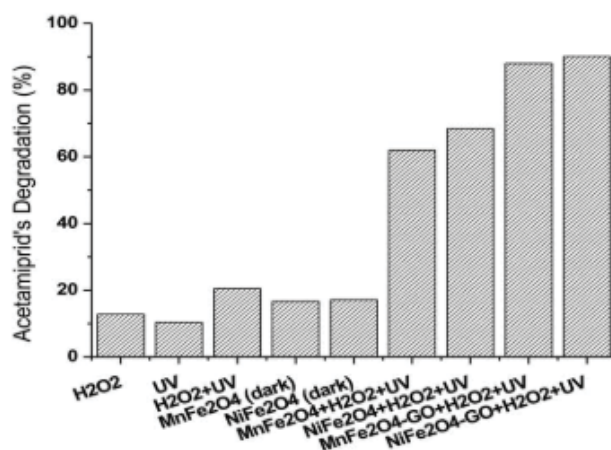
Figure 7: degradation of acetamiprid effectivity of different processes[28]

The combination of photocatalysis and oxidation by hydrogen peroxide appears to be the most efficient process. The adsorption to a catalyst, oxidation by hydrogen peroxide alone or UV photolysis alone are not enough to quantitatively remove the pollutant. Authors conclude that the process overall, if optimized, could be very useful in treatment of drinking water in which acetamiprid was present.

Even though the presence of inorganic species (which also could be present in solution) is not discussed, the study seems to provide reliable results and conclusions. The effect of scavengers (like some of the inorganic anions which could appear in solution) is also not discussed.

Kralj et al.[29] studied the photodegradation of clothianidin in water, employing TiO_2 as a photocatalyst. The impact of dissolved oxygen, nitrates and humic acids is also object of discussion. Photocatalytic experiments were performed by using a photoreactor and employing UV radiation with maximum of emission at 355 nm, and dissolving clothianidin in ultrapure water. An oxygen purge was employed to mix the reagent and the catalyst together. Analysis of the generated products was performed by using HPLC-UV measurements, while identification of products was possible employing LC-MS and LC-MS/MS techniques.

Photocatalytic degradation of the neonicotinoid is first studied. Experimental results show that photodegradation in pure water is more efficient than in water containing nitrates or humic acids. The explanation to this fact could be the scavenger effect of these substances on hydroxyl radicals generated during the photocatalysis. Those substances could react with them, so less hydroxyl radicals would be present in solution and therefore few oxidation reactions could occur. The additional effect of humic acids acting as inhibitors of the degradation process (as explained in *Figure 4*) must be considered as well.

A study of the toxicity of the generated products was performed. The parameter of interest was the bioluminescence of *Vibrio fischeri*[27], a marine bacterium which is profusely used in ecotoxicological evaluations of wastewaters and soils. The generated products may inhibit the bioluminescence of this bacteria in a higher or lower extent depending on its high or low toxicity. Products generated by photocatalysis in presence of humic acids appear to be less toxic than the ones generated in presence of nitrates or pure water: the inhibition of bioluminescence by the first ones is approximately the half of the second ones.

Authors do not consider factors like the optimization of catalyst concentration, the effect of other inhibitors (like carbonate ions), the impact of initial concentration of clothianidin, or the temperature at which the photodegradation occurs. They conclude that the process is far from being optimal, even though the presence of humic acids may reduce the toxicity of the generated products. However, they do identify different species generated by the degradation of the pesticide by application of LC-MS techniques (8 different products with *m/z* ratios ranging from 96,0557 to 218,0025 were identified), so their work could be useful in the mechanistic study of the degradation of clothianidin.

Photo Fenton Method

A method of special interest is UV-enhanced Fenton Process, which is based in the generation of hydroxyl radicals ($HO^\bullet$) by reaction of Fe^{2+} species with hydrogen peroxide. Conventional Fenton process (in absence of radiation) is based in the degradation of pollutants by iron redox reactions and may be described in the following way:

$$Fe^{2+} + H_2O_2 \rightarrow HO^\bullet + Fe^{3+} + OH^-$$

Reaction 15: oxidation of Fe^{2+} in presence of hydrogen peroxide

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+$$
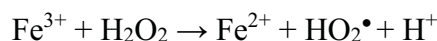
Reaction 16: reduction of Fe^{3+} to yield hydroperoxyl radicals

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^-$$
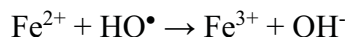
Reaction 17: oxidation of Fe^{2+} by a hydroxyl radical

This process yields hydroxyl radicals, which, as it has been previously discussed, have a high redox potential and can oxidize the molecules of interest.

In presence of light, the generation of hydroxyl radicals is enhanced by two mechanisms: homolytic cleavage of the O-O bond in hydrogen peroxide and reduction of Fe^{2+} in presence of water. Reactions 18 and 19 summarize the process:

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet$$
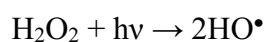
Reaction 18: homolytic cleavage of hydrogen peroxide

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^\bullet + H^+$$
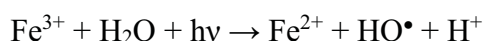
Reaction 19: reduction of Fe^{3+} in aqueous medium

As it can be seen, the radiation plays a catalytic role: the iron (III) species is reduced to yield Fe^{2+}, thus being able to restart the cycle[30].

Photo-Fenton method is subjected to the optimization of several parameters, such as the concentration of hydrogen peroxide and the ferrous salt, as well as the pH and the wavelength of the employed radiation. Other factors, like the concentration of species

which react with hydroxyl radicals disabling the oxidation process (the so-called *scavengers*) have also great relevance[31].

Fasnabi et al.[32] considered only one neonicotinoid, acetamiprid, in wastewater samples. The aim of their study was to evaluate the effect of radiation when incorporated to Fenton processes.

The radiation source was a 125W medium pressure vapour lamp. $FeSO_4 \cdot 7\ H_2O$ was employed as a Fe^{2+} source, and 0,1N sulphuric acid employed to buffer the solution to the optimal value of pH (around 3).

The results obtained by Fasnabi et al. reinforce the initial hypothesis: initial quantities of the ferrous salt and hydrogen peroxide are lower than in the case of "dark" Fenton processes.

The explanation to this experimental fact is the additional formation of hydroxyl radicals (responsible for the oxidation of the neonicotinoid), by reduction of Fe^{3+} in aqueous medium and homolysis of O-O bond in hydrogen peroxide, as stated in reactions 18 and 19.

Liu et al.[33] studied the degradation of Imidacloprid in aqueous solution by photo-Fenton process. The aim of the study was to determine the experimental conditions which yielded the best mineralization results. Waste iron (II) oxide was the Fe^{2+} source.

Their method was to compare the mineralization degree of the pesticide in different conditions: in presence of the iron salt alone, employing oxygen peroxide alone, UV radiation alone, combination of both reagents, combinations of radiation with each one of the reagents, and in a system with both reagents and radiation.

Hydrogen peroxide alone could not degrade the pesticide, since its reduction potential is relatively low. Also, the iron catalyst could not efficiently reduce the concentration of organic matter, due to its low capacity of adsorption. When used together, the catalyst and hydrogen peroxide can remove 20% of total organic carbon. The interaction between these two species generates hydroxyl radicals, by oxidation of Fe^{2+} to Fe^{3+} (as seen in reaction 16).

Coupling of Hydrogen peroxide with UV radiation supposes an increase in the mineralization degree (58,3% of TOC removed). The explanation to this phenomenon may be found in the homolytic cleavage of hydrogen peroxide, an additional source of hydroxyl radicals.

If catalyst, H_2O_2 and UV radiation are employed together, nearly all organic carbon is mineralized (97,7%). This effective degradation could be explained not only by a great formation of very oxidizing hydroxyl radicals, but also by the formation of ferric carboxylate compounds (by reaction of these generated radicals with Fe^{3+}) which are then converted to Fe^{2+} aquo complexes by ligand-to-metal charge transfer reaction (further oxidation of the ligand).

The effect of O_2 purge during the process tends to increase the efficiency of the process. Molecular oxygen acts as an oxidant, which helps to nearly complete the oxidation process. The process may be explained as a peroxidation of the generated organic radicals, which may hydrolyse to yield other reactive species such as hydroperoxyl radicals ($HO_2^{\bullet}$).

Initial pH is a parameter which also has great importance, since it is related to the interaction of the iron catalyst with the solution but also the generation of reactive oxygen species (since hydroxyl anions may complex iron and absorb radiation, generating hydroxyl radicals). The relation between total organic at any time and in the beginning of the experiment was measured in a pH range of 3.0 to 5.0, and an optimal value of pH of 3.5 was obtained.

The effect of initial concentration of hydrogen peroxide was studied as well. The efficiency of the process (measured by the total organic carbon which is removed) increased as the concentration of this oxidant species was greater, until a certain concentration (125.5mM), where it started to decrease. The explanation to this phenomenon may be the reaction of hydroxyl radical with excess hydrogen peroxide, rather than with organic matter.

The authors concluded that the ideal conditions for the removal of imidacloprid in wastewater involved photocatalysis with iron oxide as a catalyst (5.0 g/L) in presence of hydrogen peroxide (105mM), at a pH value of 3,5 and with an O_2 current as an auxiliary species. In these conditions, TOC could be removed in a 97,7% in a lapse of 6h. However, the study does not contemplate the presence of inorganic species or hydroxyl scavengers which could affect any of the parameters discussed above.

Ozonation

Ozone is a powerful reagent for the oxidation of organic matter. This unstable oxygen allotrope has a relatively high standard reduction potential (2,07V) [34], which permits the oxidation of an elevated number of compounds, with reaction products being as innocuous as water and oxygen.

In aqueous medium, ozone reacts with water, yielding superoxide radical anions and hydroxyl cations:

$$O_3 + H_2O \rightarrow 2O_2^{\bullet-} + 2H^+$$
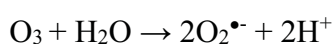
Reaction 20: Generation of superoxide anionic radicals by aqueous ozone reaction

As previously discussed in reactions 10,11 and 18, superoxide anion yields hydroxyl radicals (HO$^\bullet$).

Another reaction pathway would involve the generation of stable molecular oxygen plus an atomic O$^\bullet$ radical:

$$O_3 \rightarrow O_2 + O^\bullet$$
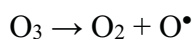
Reaction 21: Generation of atomic oxygen radicals

O$^\bullet$ atomic radicals are unstable by nature, and react with water in aqueous medium yielding hydroxyl radicals:

$$O^\bullet + H_2O \rightarrow 2\ HO^\bullet$$
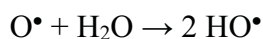
Reaction 22: Generation of hydroxyl radicals by reaction of O radical with water

Ozonation is, like the other discussed methods, subjected to several improvements or adjustments, such as the incorporation of UV radiation or auxiliary oxidants (like hydrogen peroxide). The employment of ozone and hydrogen peroxide combined is often referred as "peroxone".

Cruz-Alcalde et al.[35] discussed the removal of acetamiprid by ozonation. Their approach consisted in the mixing of aqueous ozone solutions, prepared by the bubbling of an ozone/oxygen mixture. The temperature of the medium was maintained at 10±1ºC during the preparation of the solutions, and 25±1ºC during the degradation experiments. The side effects (adsorption, photolysis, hydrolysis) were controlled in different ways: aluminium foil covered the beakers to avoid the influence of light, pH was buffered in different values ranging 2-7 and different plastic materials were in contact with solutions of pesticide to monitor its adsorption to them. HPLC-DAD was employed to determine the

concentration of pesticide. The degradation products were analysed by LC-MS. Finally, toxicity assays based in the inhibition of light emission by bacteria *Vibrio Fischeri*[27] were carried out, in order to evaluate the toxicity of the generated products.

Results show that acetamiprid does not react directly with ozone, but it does react with hydroxyl radicals. When a radical scavenger (tert-butyl alcohol) was added, the concentration of the pollutant remained nearly constant, while the absence of scavenger allowed the virtually full degradation of acetamiprid with doses of ozone of about 5 mg/L. The kinetics of the process were obtained to be second order, with value of the rate constant equal to $0,25\pm0,02$ $M^{-1}s^{-1}$.

The study does not consider the effect of inorganic species (such as halide, carbonate, or metallic ions present in aqueous solution). The objective of the study appears to be the identification of intermediates and reaction products, rather than the effect of the previously discussed parameters in the degradation process.

Zhao et al.[36] discussed the degradation of thiamethoxam in aqueous solution by ozonation. Their experimental work was carried out by employing a reactor fed with an ozone current, in which the aqueous solutions of thiamethoxam (of different concentrations) were set. Adjustment of samples pH was achieved by using a phosphate buffer. After regular time intervals, samples were collected for UV spectrophotometry and HPLC and LC-MS analysis.

Effect of pH in the degradation was firstly studied, since the degradation mechanism strongly depends on the pH of the system (O_3 addition at acidic pH and radical chain reactions at alkaline pH)[37]. An increase of the value of pH radically boosts the degradation yield (from 53,7% at pH=3 to 81,4% at pH=9). Further increases in pH do not boost the efficiency of the reaction (71,4% at pH=11).

When pH is low, ozone molecules are stable in solution, and the degradation of the organic molecule strongly depends on its chemical nature (since not all organic pollutants

undergo nucleophilic or electrophilic addition of ozone). As pH rises, O_3 decomposes yielding $HO^\bullet$ radicals, which are far less selective oxidants, thus increasing the degradation yield.

The impact of the initial concentration of pollutant is object of study. Experimental results showed that the total degradation yield decreased as the initial concentration of the pollutant increased. Authors conclude that this experimental fact is explained by stoichiometric reasons: a certain O_3 concentration is available for a determined flux. For this reason, as initial concentration of the pollutant increases, less ozone will be available for reaction.

For the same reason, degradation yield is directly proportional to the initial concentration of O_3. However, this proportion is not linear: at concentrations above 20,1 mg/L of ozone, the degradation rate only increases slightly. An explanation to this fact may be found considering that, at low ozone concentrations, an increase in the oxidant concentration favours the mass transfer from the gas to the liquid phase, thus increasing the available concentration of ozone for degradation. At higher ozone concentrations, there is an excess of this substance in solution which may impede the correct reaction with the pollutant. Economical and technical reasons (since O_3 generation is not cheap and may damage the equipment) must be considered as well.

The influence of temperature is then considered. When it increases from 293 to 303K, the degradation yield rises from 65,1 to 80,0%, which boosts to 88,8% when the value of temperature is equal to 309K. Further increases of temperature decrease the efficiency of the degradation, even though solubility of ozone in solution is higher.

This study does not consider the effect of dissolved organic matter or inorganic species in solution (solutions of thiamethoxam are prepared in Milli-Q water), and it is not focused on the impact of auxiliary methods (employment of UV radiation, addition of hydrogen peroxide), frequently used to enhance the degradation efficiency.

Conclusions/Conclusións/Conclusiones

After reviewing the different advanced oxidation procedures (AOPs), some conclusions may be extracted:

Methods involving UV direct photolysis tend to be the most effective in terms of mineralization: they quantitatively oxidize pollutants to CO_2, NO_3^-, PO_4^{3-}, SO_4^{2-}… Furthermore, this process tends to be kinetically fast, so virtually full mineralization may be achieved in relatively short times. However, these methods are usually expensive (continuously producing energetic radiation is a high-cost operation) and involve safety measures (since the employed radiation is ionizing).

Photosensitized degradation-based methods are generally cheaper (the employed radiation may be less energetic) but they involve the use of (at least) one auxiliary substance, the photosensitizer. Handling of this species may even be hazardous (for example, molecular chlorine). Products generated using this technique can also be more dangerous than the starting material, as this process is not so efficient in terms of degradation as direct photolysis.

Photocatalysis is a good alternative: degradation yields are more than acceptable, several catalysts are commercially available or may be easily synthetized, and some methods even allow sunlight as the radiation source. Inconveniences of this method could be the optimization of several parameters: pH, concentration of auxiliary oxidants and catalyst, presence of hydroxyl scavengers, dissolved organic matter and inorganic species, temperature... The same parameters should be taken into consideration for Photo-Fenton method (specially, pH, since Fe $(OH)_2$ could precipitate in solution), even though this procedure also presents advantages in terms of degradation effectivity, prize and reaction rates.

Ozonation could be the less effective method of the ones reviewed in this work. Even though the degradation yields may be relatively high (up to around 90%), this approach requires constant production of ozone and relatively stable conditions (buffered pH and stable temperature). Literature reviewed in this work does not take into consideration crucial factors as presence of hydroxyl scavengers, inorganic species or dissolved organic matter, so it is not possible to assure the efficiency of this process.

In conclusion, it appears that Photocatalysis and Photo-Fenton method are the most relevant approaches, as they combine effectivity and efficiency with relatively low prizes. UV direct photolysis (generally, supported by auxiliary species as hydrogen peroxide) would be the method of choice to maximize mineralization at any cost.

However, it must be taken into consideration that this work reviews AOPs in laboratory conditions *i. e.* the small scale. Further studies should be carried out to assess the effectivity of these methods in large wastewater treatment plants.

Tras avaliar os diferentes POA, pódense extraer as seguintes conclusións:

Os métodos baseados na fotólise UV directa adoitan ser os máis efectivos en termos de mineralización: oxidan cuantitativamente os contaminantes a CO_2, NO_3^-, PO_4^{3-}, SO_4^{2-}, etc. Ademais, este proceso acostuma ser cineticamente rápido, polo que practicamente toda a mineralización podería acadarse en intervalos de tempo relativamente curtos. Porén, estes métodos son, polo xeral, caros (xa que a produción continua de radiación enerxética é unha operación de alto custe) e adoitan implicar o uso de medidas de seguridade (debido a que a radiación de traballo é ionizante).

Métodos baseados na degradación fotosensibilizada son, polo xeral, máis baratos (a radiación de traballo pode ser menos enerxética) mais precisan (polo menos) dunha substancia auxiliar, o fotosensibilizador. O manexo desta(s) substancia(s) pode ademais ser perigoso (como, por exemplo, o gas cloro). Produtos xerados empregando esta técnica poden ser máis perigosos que o material de partida, xa que este proceso non é tan efectivo en termos de mineralización como a fotólise directa.

A fotocatálise é unha boa alternativa: os rendementos da degradación son máis que aceptables, existen diversos catalizadores que están dispoñibles comercialmente ou poderían ser sintetizados con facilidade, e algúns métodos até permiten o uso de luz solar como fonte de radiación. Como inconveniente deste procedemento poderíase citar a optimización de varios parámetros: pH, concentración de oxidantes auxiliares e catalizador, presenza de eliminadores de radicais hidroxilo, materia orgánica disoluta e especies inorgánicas, temperatura... Os mesmos parámetros deberían ser considerados para o método Photo-Fenton (especialmente o pH, xa que o Fe $(OH)_2$ podería precipitar en disolución), aínda que este procedemento posúe tamén vantaxes en termos de efectividade da degradación, prezo e velocidades de reacción.

A ozonización podería ser o método menos efectivo dos que se revisan neste traballo. Aínda que os rendementos da degradación asociados a este proceso poden ser relativamente altos (até un 90%), este procedemento require a produción constante de ozono e condicións relativamente estables (pH fixo e temperatura constante). A bibliografía revisada neste traballo non considera factores cruciais como a presenza de eliminadores de radicais hidroxilo, especies inorgánicas ou materia orgánica disoluta, polo que non é posible asegurar a eficiencia do proceso.

En conclusión, a Fotocatálise e o método Photo-Fenton semellan os métodos máis destacados, xa que combinan eficacia e eficiencia con prezos relativamente baixos. A fotólise UV directa (normalmente en presenza de especies oxidantes como o peróxido de hidróxeno) pode ser tamén un bo método para maximizar a mineralización a calquera prezo.

Non obstante, é preciso destacar que este traballo avalíanse procesos de oxidación avanzada (POA) en condicións de laboratorio (isto é, a pequena escala). Estudos posteriores deberían ser levados a cabo para determinar a efectividade destes métodos en grandes estacións de tratamento de augas residuais.

Tras llevar a cabo la evaluación de Procesos de Oxidación Avanzados (POA), se pueden extraer algunas conclusiones.

Los métodos que se basan en la fotólisis UV directa suelen ser los más efectivos en términos de mineralización: oxidan cuantitativamente los contaminantes a CO_2, NO_3^-, PO_4^{3-}, SO_4^{2-}… Además, este proceso suele ser cinéticamente rápido, por lo que prácticamente toda la mineralización podría alcanzarse en intervalos de tiempo relativamente cortos. Sin embargo, estos métodos son generalmente caros (puesto que la producción de radiación energética de forma continua es una operación de alto coste) y suelen conllevar el uso de medidas de seguridad (ya que la radiación de trabajo es ionizante).

Los métodos que implican el proceso de degradación fotosensibilizada son, por regla general, más baratos (la radiación de trabajo puede ser menos energética) pero necesitan de (por lo menos) una sustancia auxiliar, el fotosensibilizador. El manejo de esta(s) sustancia(s) puede además ser peligroso (como en el caso de gas cloro). Los productos generados mediante el empleo de esta técnica podrían ser más peligrosos que el material de partida, puesto que este método no es tan efectivo en términos de mineralización como la fotólisis directa.

La fotocatálisis es una buena alternativa: los rendimientos de la degradación son más que aceptables, existen diversos catalizadores que están disponibles comercialmente (o podrían ser sintetizados con facilidad) y algunos métodos hasta permiten el uso de luz solar como fuente de radiación. Como inconveniente de este procedimiento se podría mencionar la optimización de diversos parámetros (pH, concentración de oxidantes auxiliares y catalizador, presencia de eliminadores de radical hidroxilo, materia orgánica disuelta y especies inorgánicas, temperatura…). Los mismos parámetros deberían ser considerados para el método Photo-Fenton (especialmente, el pH, puesto que el $Fe(OH)_2$ podría precipitar en disolución), aunque este proceso presenta también ventajas en términos de efectividad de degradación, precio y velocidad de reacción.

La ozonización podría ser el método menos efectivo de los que se evalúan en este trabajo. Aunque los rendimientos de degradación pueden ser relativamente altos (hasta de un 90%), este procedimiento requiere de una producción constante de ozono y de condiciones relativamente estables (pH tamponado y temperatura constante). La bibliografía revisada en este trabajo no tiene en cuenta factores cruciales como la presencia de eliminadores de radical hidroxilo, especies inorgánicas o materia orgánica disuelta, con lo que no es posible garantizar la eficiencia de este proceso.

En conclusión, la Fotocatálisis y el método Photo-Fenton parecen los métodos más relevantes, puesto que combinan eficacia y eficiencia con precios relativamente bajos. La fotólisis UV directa sería el método elegido si se necesitase maximizar la mineralización sin importar el coste.

No obstante, debe tenerse en cuenta que este trabajo evalúa procesos de oxidación avanzada (POA) en condiciones de laboratorio (es decir, a pequeña escala). Estudios posteriores deberían ser llevados a cabo para determinar la efectividad de estos métodos en grandes estaciones de tratamiento de aguas residuales.

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