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Use of recycle waste metal shavings as catalysts for advanced oxidation process applied to water treatment

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All our dreams can come true if we have the courage to pursue them.

Walt Disney

Llegar a este punto es ver la luz al final de un túnel, uno que muchas veces parecía que fuera algo muy lejano. En esta trayectoria he tenido la gran suerte de conocer a personas increíbles, de vivir experiencias nuevas y sobretodo aprender de todos y con todos. Seguramente será muy tópico decirlo, pero esto lo he conseguido gracias a todo el apoyo constante de mis amigos, y familia. Por creer en mí cuando yo no podía y por darme un empujón cuando más lo he necesitado.

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CONTENTS

SUMMARY

In the last decades, the great industrial and demographic development has led to an unsustainable increase in the consumption of energy and raw materials that negatively affects the environment. This entails an increase in waste and generated contamination, especially organic micropollutants that require specific treatments in addition to a high operating cost. Therefore, alternatives and low cost treatments are studied these days in order to eliminate them effectively and avoid potential risks to the environment and human health.

Advanced Oxidation Processes (AOPs) are based on their ability to generate hydroxyl radicals (HO·). The combination of an oxidizing agent (*e.g.* H_2O_2), a catalyst (*e.g.* Fe (II)) and energy (*e.g.,* UV radiation) produce this species with a high oxidation potential, which is capable of oxidizing most compounds in a non-selectively way. In this project, we used metal-based catalysts for promoting Fenton-like reaction in acidic or neutral pH to wastewater treatment. It is used to complete mineralization of the pollutants or their degradation in more easily biodegradable substances. The intention is to develop an effective alternative for elimination of the organic contaminant of the effluents and to test the use of a low-cost abundant product (waste metal shavings from metalworking industry) from an economic and environmental point of view.

Zero Valent Iron (ZVI) and waste metal shavings (WMS) from metalworking industry are used as a catalysts and Sulfamethoxazole (SMX) was selected as model emerging pollutant in synthetic water. It is studied the different variables to optimize this Fenton-like process as the conditions of the catalysts and their most optimal concentration.

Fenton oxidation as a combination of waste metal shavings with H_2O_2 at acid pH to generate hydroxyl radicals is a potential alternative or a complementary solution to conventional wastewater treatment processes for industrial wastewater treatment. An advantage it is that the waste metal shaving can be used over without requiring regeneration or replacement and can be removed from the treated water by sedimentation or filtration.

Keywords: Advanced Oxidation Processes, Fenton, Sulfamethoxazole, waste metal, ZVI, Fenton-like.

RESUMEN

En las últimas décadas el gran desarrollo industrial y demográfico ha llevado a un aumento insostenible del consumo de energía y materias primas que afecta negativamente al medio ambiente. Esto conlleva un aumento de residuos y contaminantes generados los cuales requieren tratamientos específicos además de un elevado coste de operación. Por ello, hoy en día se estudian alternativas y tratamientos de bajo coste para poder eliminarlos de forma efectiva y no supongan un riesgo para el medio ambiente y la salud humana.

Los procesos de oxidación avanzada (POA) consisten en su capacidad para generar radicales hidroxilo (HO·). La combinación de un agente oxidante (H_2O_2), un catalizador (Fe (II)) y energía produce esa especie con un alto potencial de oxidación capaz de oxidar compuestos orgánicos de forma no selectiva. En este caso, utilizaremos catalizadores metálicos en la aplicación de POAs para el tratamiento de aguas residuales simuladas. Los POA seleccionados para la ocasión fueron procesos tipo Fenton con un pH cercano a la neutralidad o ácido, que normalmente se utilizan para completar la mineralización de los contaminantes o su degradación en sustancias más fácilmente biodegradables. La intención es desarrollar una alternativa efectiva para la eliminación de la materia orgánica de los efluentes y probar el uso de un producto abundante de bajo costo (virutas de hierro y desechos de la industria metalúrgica), lo cual resulta interesante desde un punto de vista económico y ambiental.

En este proyecto se utiliza hierro cerovalente (ZVI) y residuos metálicos de la industria metalúrgica como agente catalizador, además desulfametoxazol como contaminante emergente modelo a tratar en agua residual sintética. Se estudian las diferentes variables para optimizar el proceso tipo Fenton, como el pH del medio o la concentración de catalizador que conduce a un proceso más efectivo.

La oxidación Fenton como una combinación de virutas de metal residuales con H_2O_2 a pH ácido para generar radicales hidroxilos es una solución alternativa o complementaria a los procesos convencionales de tratamiento de aguas residuales para el tratamiento de aguas residuales industriales. Una ventaja es que las virutas de metal se pueden usar sin necesidad de regeneración o reemplazo y se puede eliminar del agua tratada por sedimentación o filtración.

Palabras clave: Procesos de oxidación avanzada, Fenton, Sulfamethoxazole, residuos metálicos, ZVI, Fenton-like.

1. INTRODUCTION

1.1. EMERGING CONTAMINANTS (ECS)

Currently, one of the biggest challenges worldwide is to preserve freshwater resources. Since the beginning of the Industrial Revolution, the environment (including aqueous compartments,) has suffered the continuous introduction of trace amounts of human-made organic substances employed in daily human activities, such as pesticides, pharmaceutical compounds, personal care products, etc. During the last decades, with the development of highly sensitive analytical techniques, these substances have been detected in water bodies worldwide. Moreover, and thanks to advances in Toxicology, it is nowadays known that the exposure to these chemicals can pose risks to human health and the environment. More of these contaminants have no reglamentation for treatements on water. These are the so-called emerging contaminants. [1]

Wastewater contains residual organic material, which has to be removed before being discharged to a flow of natural waters. This is typically done in wastewater treatment plants (WWTP). One of the most important kind of effluents to be treated due to its high content of organic compounds, toxic or harmful to the environment are those that comes from the chemical industry for which minimum quality requirements are established by law. The main treatments that are carried out in a wastewater treatment plant are: pre-treatment, primary treatment (or mechanical) which eliminate more than 30% of the organic matter content, including suspended particles, through physicochemical processes, and secondary treatment (or biological) to oxidize the biodegradable organic material that is dissolved in the water. However, in recent years the high consumption and industrial production have increased the percentage of emerging pollutants that nowadays circulate through the waters. These compounds are mostly unknown or uncontrolled contaminants. In comparasion with biodegradable material, both compound are organics but EC can not be degraded by conventional treatments. [2][3]

Water purification methods are often not effective with respect to the removal of organic emerging contaminants. Therefore, tertiary treatments arise to further polishing a treated water.

It is a type of treatment more expensive than the previous ones and it is used in special cases when they need a specific grade of purity because of law enforcements, usually in the case of industrial effluents. Some processes used as tertiary treatments are ion exchange resins, adsorption on activated carbon, ultrafiltration, reverse osmosis, electro-disinfection, ceramic membranes, advanced oxidation, etc.

1.2. LEGAL FRAMEWORK

As mentioned previously, the concern with emerging pollutants is increasing. After a legislative resolution in the European Union (pioneering in the protection and reuse of water) Directives 2000/60 / EC and 2008/105 / EC were launched and some years after were amended with regard to priority substances in the field of water policy. The result of this process was Directive 2013/39 / EU of the European Parliament and of the Council of August 12, 2013. In general, this regulation promotes:

- The identification of the causes of pollution, as well as treating the emissions of pollutants at the source, the most efficient way in economic and environmental terms.
- The Identification of those priority substances occurring in the aquatic environment potentially posing a significant risk to human health and the environment.
- Preventive action in front environment and the polluter-pays principle.
- The development of innovative water/wastewater treatment technologies. [4][5]

In these directives, a list of priority substances (organic pollutants) in the field of water policy is included. Among them, there are some pharmaceuticals such as SMX, the compound that we used in the present work. The table belong shows some parameters associated to this study.

Table 1. Maximum pollution parameters of authorized discharges (Article 6) [6]

Propriety/material	Value or range of values
Temperature	**<40ºC**
pH	6 - 9
Colour	Inappreciable in solution 1/40
Conductivity	5000 µS/cm
Suspended solids	1.000 mg/L

Sedimentable matter	10 ml/L
DBO_5	1.000 mg/L
DQO	1.600 mg/L
Iron (Fe)	10 mg/L

Concerning the micropollutant selected for this study, there is no any legislation in Spain considering its presence in freshwater resources or wastewater matrices. There are however, some laws at European level considering some individual or chemical families, among which some antibiotics are considered: 2015/495/EU of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council; and commission implementing decision 2018/480/EU Having regard to the Treaty on the Functioning of the European Union and having regard to Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. [7]

Sulfamethoxazole is an antibiotic widely used for humans and veterinary animals, among the most frequently detected antibiotics in the aquatic environment. This antibiotic in the environment may cause adverse effects to the microbial communities, hence imposing great risk to the non-target species in the ecosystems. A general concern for public health is the development of antibiotic resistance from chronic exposure to antibiotic contaminated water. [8]

1.3. ADVANCED OXIDATION PROCESSES (AOPS)

Today there is growing interest in the study and application of the so-called Advanced Oxidation Processes (AOPs). These are more expensive than conventional technologies, but with a high proven efficiency when additional polishing steps such as disinfection or organic micropollutants oxidation are required in water treatment. Due to the high reactivity of the chemical species typically involved in AOPs (*e.g.*, hydroxyl radicals), it is certainly possible to eliminate organic and inorganic pollutants that otherwise passes WWTPs without being effectively removed. The presence of ECs and potentially associated toxicity is thus reduced, in addition to the typical reduction of biodegradable organic material (COD/TOC). It is usually applied at small or medium scale treatments and can be used alone or combined with other methods. It can also be applied to contaminated air and soils. There are many types of AOPs, depending on the agents that are used to generate hydroxyl radicals. These, however, are typically based on the use of some oxidants combined, an oxidant with a catalyst, an oxidant with radiation, radiation with a catalyst…and can be homogeneous or heterogeneous chemical processes. In the figure below, the different existing AOPs there are presented. All have in common the goal of generating hydroxyl radicals and thus oxidize target emerging pollutants.

Hydroxyl radicals, with a high oxidation capacity (redox potential of 2.8V) and unselective character, are capable of degrading most organic chemical species found in wastewater or the environment. They are also able of mineralizing these organic compounds, transforming them to compounds such as carbon dioxide and water. However, complete mineralization of emerging pollutants rarely occurs and transformation products from the oxidation of the starting compound are instead formed. [9]

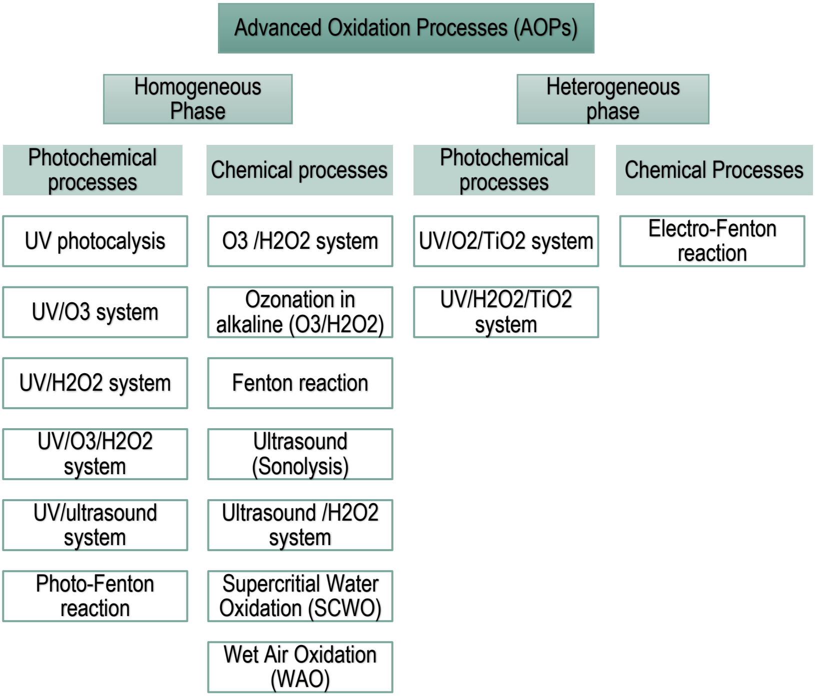


Figure 1. Major types of Advanced Oxidation Processes. [10]

1.4. FENTON PROCESS

Fenton's reaction is an oxidation process that was firstly proposed by H. J. H. Fenton (1894) for the oxidation of tartaric acid. The method is based on the generation of hydroxyl radicals ($HO\cdot$), achieved by the combination of hydrogen peroxide (H_2O_2) and iron (II) salts.

The Fenton process is a complex radical chain-type mechanism that is still under intense and controversial discussion. The pathways by which hydroxyl radicals are produced consist in general of a number of cyclic reactions involving Fe(II) or Fe(III) cations, H_2O_2 and other O and H intermediates. These ionic species are continuously oxidized-reduced during the process, allowing a sustained production of radicals $HO\cdot$ from H_2O_2 decomposition. Table 2 shows the main reactions.

Table 2. Radical chain mechanism of Fenton Process. [9][11]

Initiation	$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO\cdot$	Eq. 1.1
	$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2\cdot + H^+ \rightleftarrows Fe(II) + HO_2\cdot + H^+$	Eq. 1.2
	$H_2O_2 \rightarrow H_2O + ½\, O_2$	Eq. 1.3
Propagation	$HO\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O$	Eq. 1.4
	$HO_2\cdot + H_2O_2 \rightarrow HO\cdot + H_2O + O_2$	Eq. 1.5
Termination	$HO\cdot + Fe(II) \rightarrow Fe(III) + OH^-$	Eq. 1.6
	$Fe(III) + HO_2\cdot \rightarrow Fe(II) + O_2 + H^+$	Eq. 1.7
	$Fe(II) + HO_2\cdot + H^+ \rightarrow Fe(III) + H_2O_2$	Eq. 1.8
	$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$	Eq. 1.9

Formation of hydroxyl radicals is achieved through decomposition of hydrogen peroxide caused by iron species, which change its oxidation state from Fe(II) to Fe(III). After Fe(II) decomposes hydrogen peroxide, formed hydroxyl radicals can react with any chemical species in solution, including target organic pollutants but also those species involved in the Fenton process, ultimately leading to further radical formation (propagation reactions) or radical-chain termination, with subsequent oxidation and/or regeneration of iron species and H_2O_2. In addition, Fe (III) formed during the process can react with hydrogen peroxide, giving rise to an additional initiation pathway and Fe(II) regeneration. This process is called Fenton-like, as it is initiated by an iron species different than Fe(II). It is important to mention that it has slower kinetics than Fenton process.

The global mechanism is based on catalytic reactions. To do this, it is typically necessary that hydrogen peroxide is in excess with respect to the amount of iron added. The ratio of the different reagents is one of the aspects of interest in the present study.

It is important carrying out reactions at pH values close to 3 because under these condition the $[Fe(OH)]^{2+}$ complex becomes the predominant stable specie in solution and the reaction catalyst. On one hand, if the process is conducted at pH values lower than 3, Fe (III) ion predominates, and this is not convenient for the kinetics of the reaction. On the other hand, if pH is riseed to values higher than 3, precipitates of iron could appear. At circumneutral pH values, thus, Fe(III) would be present as iron hydroxide(precipitate). (Figure 2) [12].

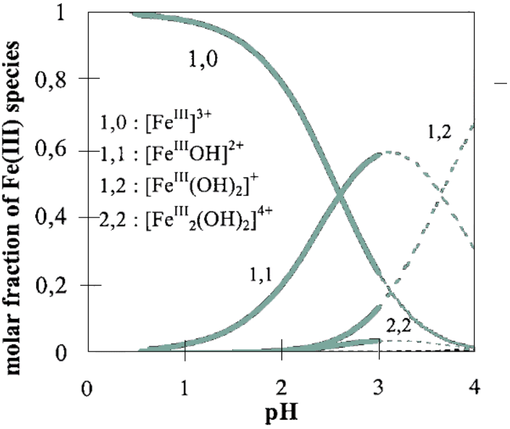


Figure 2. Speciation of Fe (III) species in acidic aqueous solution.
(Source: H. Gallard et al, 1999.) [12]

If only the main reagents (*e.g.*, iron and hydrogen peroxide) are considered, the Fenton Fenton process is considered as a process potentially convenient and economic due to the generation of oxidizing species for the degradation of several compounds. Moreover, the cheapness of hydrogen peroxide together with the harmless of potential residual on the environment make the application of H_2O_2 based processes particularly convenient. Additionally, the extra benefit due to the enhanced production of hydroxyl radicals when employing iron species (really cheap and not toxic as well) point more out these advantages. However, the necessity of working under such extreme pH conditions (~3) is the main inconvenient for Fenton processes in water and wastewater treatment. Moreover, water and wastewater need to be returned to its natural pH value, which is typically between 6 and 8. And the operational costs rise up significantly with the acid addition. Thus, the dosing of an alkali is also required after treatment.

Another disadvantage, although common for all AOPs, is the presence in solution of inorganic anions such as phosphate, chloride, nitrate, etc. These can scavenge hydroxyl radicals or cause a complexation reaction with iron, decreasing the ability of Fe(II) to dissociate H_2O_2 and thus stopping the cycle. [13]

Currently, possible alternatives to carry out the Fenton reaction without having to work with acid solutions are still under study, as iron precipitation is wanted to be avoided. Some authors have studied the possibility of adding humic substances to keep the iron complexed, as well as the use of alginates or other heterogeneous catalysts for similar purposes. In our case we use as a catalyst Zero-Valent Iron (ZVI), more specifically waste metal shavings (WMS) as a possible solution to perform Fenton and Photo-Fenton reactions at different pH conditions.

1.4.1. Photo-Fenton process

Photo-Fenton (Fe(II)/H2O2/*uv*) is a Fenton based process in which irradiation with natural (sunlight) or an artificial light source is employed to enhance the contaminant removal rate by promoting the reduction of Fe(III) to Fe(II) for decomposing hydrogen peroxide and enhancing hydroxyl radical generation. Being so, this variant of the Fenton process is kinetically faster than original or dark Fenton reaction. The Photo-Fenton process allows the generation of $HO\cdot$ through the mechanisms showed in Table 3.

Table 3. Mechanism of Photo-Fenton process [10][11]

Decomposition of hydrogen peroxide with Fe(II) catalyst	$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO\cdot$	Eq. 2.1

Incidence of radiation to make the hydrogen peroxide decomposition into hydroxyl radicals	$H_2O_2 + h\nu \rightarrow 2HO\cdot$ $Fe\ (III) + H_2O_2 + h\nu \rightarrow Fe\ (II) + HO\cdot + H^+$ $Fe(OH)_2 + h\nu \rightarrow Fe\ (II) + HO\cdot$	Eq. 2.2 Eq. 2.3 Eq. 2.4
Fe (II) regeneration	$Fe(RCO_2)]^{2+} + h\nu \rightarrow Fe\ (II) + CO_2 + R\cdot$	Eq. 2.5

2. JUSTIFICATION

Nowadays, the presence of emerging pollutants in aquatic ecosystems is of concern. There are no clear regulations on this subject, but there is increasing evidence of the risks that these substances can entail for human health and the environment. In addition, and although they pass through water and wastewater treatment plants, these pollutants are not effectively eliminated since the conventional technologies are not designed to that purpose. Therefore, alternatives must be sought for their effective elimination. A group of processes with a lot of potential for this objective would be AOPs. [14][15]

The Fenton process is a very effective AOP in the degradation of organic matter and in particular of emerging contaminants. It is a simple and apparently low cost process, but the need of working at acidic pH conditions is an important drawback.

Recent studies suggest that ZVI combined with hydrogen peroxide generates hydroxyl radicals capable of oxidizing organic compounds, even at circumneutral pH (5-6). Therefore, it want to be tested if the process could be carried out with waste metal shavings made of iron (i.e., ZVI), considered a residue in the metallurgical industry. [12]

3. OBJECTIVES

The principal objective of this project is to study and test the use and effectiveness of waste iron shavings as "low cost" catalyst in advanced oxidation processes, particularly in Fenton-like systems. There is a lot of bibliography related to the Fenton process but none of them uses waste metal shavings from metallurgical industry as catalyst. In addition, it will be compared the process performance with that for the classic Fenton process and Fenton reaction catalysed with ZVI. To accomplish these general objectives, the following specific objectives were also established:

- To compare the degradation of the drug SMX under different pH conditions for the processes tested, including circumneutral pH.
- Evaluate the optimal doses of different chemical reagents (Fe(II), H_2O_2), processes corresponding to the degradation of SMX.
- Proving the effectiveness of ZVI and waste metal shavings as catalysts.
- Test the reusability of waste metal shaving.
- Estimating the economic costs of the process.

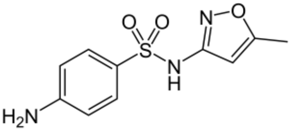
4. MATERIALS AND METHODS

4.1. CHEMICALS AND REAGENTS

4.1.1. Pollutant agent, Sulfamethoxazole

Sulfamethoxazole (SMX) is an antibiotic agent that interferes with folic acid synthesis in susceptible microorganisms. Its broad spectrum of activity has been limited by the development of bacterial resistance [16]. In this work, analytical grade SMX was purchased from Sigma-Aldrich Chemical Co (Germany).

Table 4. Sulfamethoxazole properties).

Propriety	Value
Molecular formula	$C_{10}H_{11}N_3O_3S$
Molecular structure	
Molecular weight [g/mole]	253.276
CAS No.30	723-46-6
Melting Point [^{0}C]	167
Water solubility [mg/L]at 37 °C	610
pKa	9.45
log Kow	-0.45 (pH 2.0)

The standard curve for SMX determinations by HPCL can be found in the Appendix. (Figure 16)

4.1.2. Zero-Valen Iron (ZVI) and Waste metal shavings

In part of the experiments carried out, waste steel (iron) shavings were tested as catalysts with the aim of making the Fenton process more economical. These were provided by Dynacast España S.A., a metalworking company.

Iron shavings were in fact a mixture of different commercial steels (THYRAPID-3343, BOHLER K720, THYROTHERM-2344 EFS and BOHLER W360) employed for mould production, which resulted in an average iron content of about 92% [18]. In fact, that is the theoretical composition of the moulds they produce, but this waste metal undergoes a mechanic treatment with cutting fluid. Because of that, prior to Fenton experiments, it must be taken the waste metal shavings and pass them through a standardized cleaning process. For this, it was used methane tetrachloride (an organic solvent used to extract extra oils, fats and waxes even in the dry cleaning of the pharmaceutical industry). Then shavings were dried in the stove.

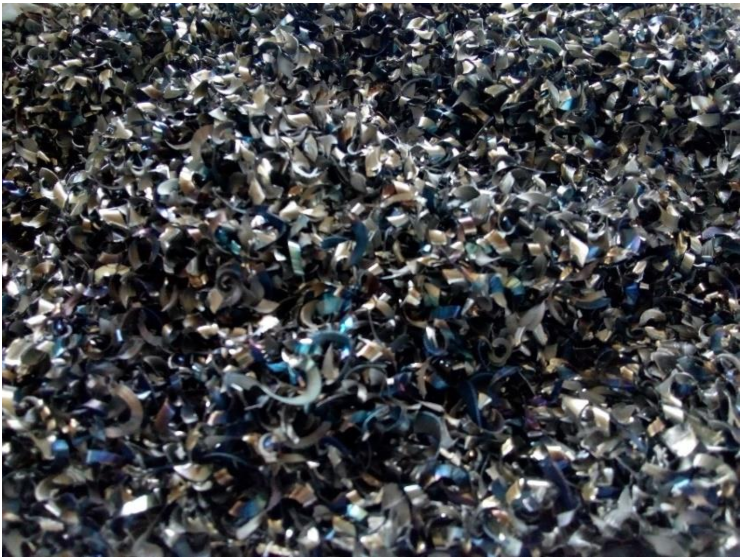


Figure 3. Photo of waste metal shavings (0.90±0.45 mm)

4.1.3. Other chemicals

Table 5. Information about reagents. [19]

Name	CAS No.	Formula	Company	Purity (%)	Used in/for
Acetonitrile	75-05-8	CH_3CN	Fischer Chemical	99.80	HPLC analysis
Ammonium metavanadate	7803-55-6	H_4NO_3V	Sigma Aldrich	99	H2O2 determination
Ascorbic acid	50-81-7	C6H8O6	Panreac Química	91	Totally Fe determination
Buffer solution	64-19-7	CH3COOH	Merck Millipore	-	Fe(II) determination
Hydrogen peroxide	7722-84-1	H2O2	Merck Millipore	30 w/w	Fenton Process
Iron ZVE (powder)	7439-89-6	Fe	Sigma Aldrich	97	Fenton Process
Methane tetrachloride	56-23-5	CCl_4	-	-	Cleaning waste metal shaving
Methanol	65-56-1	CH3OH	Panreac Química	99.90	Stop the reaction with H2O2 to HPLC
Orthophosphoric acid	7664-38-2	H3PO4	Panreac Química	85	HPLC analysis
Oxygen	7782-44-7	O2	Abelló Linde	99.9999	Fenton Process
Sulfamethoxazole (SMX)	723-46-6	C10H11N3O3S	Sigma Aldrich	-	Pollutant reagent
Sodium Chloride	7647-14-5	NaCl	Panreac Química	-	Fenton Process
Sodium hydrogen sulfite	7631-90-5	NaHSO3	Panreac Química	40 w/w	TOC
Sulfuric acid	7664-93-998	H2SO4	Panreac Química	98	For pH adjustment
1,10-phenanthroline	66-71-7	C12H8N2	Sigma Aldrich	99	Fe(II) and Fe total determination

4.2. FENTON EXPERIMENTS

4.2.1. Preparation of sample and reagents

To start each experiment, it was prepared first the mixture of the model emerging pollutant (SMX). For this, it was selected a concentration of 20 ppm of SMX. Then, the solution was kept under stirring during 24 hours. For preliminary experiments it was prepared 1L, whereas for bench reactor experiments it was used 3L at the same conditions.

In some experiments, it had to be lower the mixture pH to 2.8±0.2 using concentrated H_2SO_4. The pH measurement was made with the pH meter SenSION MM374 HACH, which was calibrated every day with pH 4, 7 and 10 standard buffers.

For Photo-Fenton process, three mercury lamps (low-pressure) BLB Philips TL 8W-08 FAM (8W electric power) were employed. The BLB UV radiation range was from 300 nm to 410 nm, having the maximum peak of light emission at 365 nm. This lamp has and approximated lifetime of 10,000 hours. Those lamps were switched on 15 minutes before the start of the reaction in order to stabilize light emission.

The water that was used for the experiments, mixtures and analyses came from a Milli-Q ® (Millipore Corporation) laboratory purification system, which consists of successive steps of filtration and deionization to achieve a high purity water. The main properties of Milli-Q water are an electrical resistivity of 18.2 MΩcm at 25 ºC, an organic carbon content below 2 ppb and pH around 5.5.

4.2.2. Procedure of experiments

During the first stage of experimentation, it was started the work by focusing on the study of the process performance according to different doses of reagents, as well as on the influence of other factors such as pH, oxygen bubbling or the presence of chloride (Cl^-) in the reaction medium. This preliminary information should be later employed when planning experiments in the 3-L reactor. (bench reactor)

Four Erlenmeyer with a volume of 200mL were employed as reactors in this part of the work. The employed concentrations of iron and hydrogen peroxide were varied according to Figure 4.

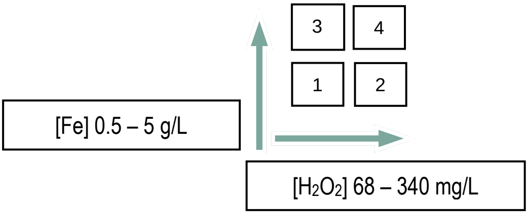


Figure 4. Preliminary model experiments distribution.

Three samples were withdrawn from each reactor at fixed reaction times of 0, 50 and 90 min. After filtration through 0.45 µm PTFE filters, residual concentrations of SMX, H_2O_2 and iron species were then determined according to the analytical methods later detailed in this report.

In total, 28 preliminary experiments were conducted. Those experiments were carried out a circumneutral pH (approximately 5.5 ± 0.5) or varying pH to optimum 2.8. Some were performed with chloride addition (10 ppm) or dry oxygen bubbling. Also, the degradation process employing waste metal shavings was tested with and without hydrogen peroxide. All experiments are explained in table 5.

The SMX degradation by Fenton under different experimental conditions lasted 90 min. The experiments were carried out in a jacketed batch reactor, with a volume of 3L, 36 cm height and 17 cm of inner diameter. The jacket was connected to a thermostatic bath to maintain the temperature at 20ºC (Tectron 3473200 SELECTA). The reactor was under constant stirring by the action of a propeller agitator (IKA Eurostar 60) which was set at 250 rpm.

Each experiment was conducted according to the following general procedure. It was introduced the model solution in the reactor after preparing it. The reaction was then initiated with the simultaneous addition of ZVI and H_2O_2 into the reactor (the concentration of that depended on each particular experiment). Samples (> 20 mL) were withdrawn at 0, 1, 5, 15, 30, 45, 60 and 90 min. These were filtered and then employed for analytical determinations. For each sample, 0.5 mL was used for SMX determination, 4 mL for Fe(II) and total iron monitoring, 1.5 mL for H_2O_2 evolution and 14mL for TOC determination.Reactor Device is shown in the figure 5 for Bench reactor (including de mercury lamps for Foto-Fenton reaction).

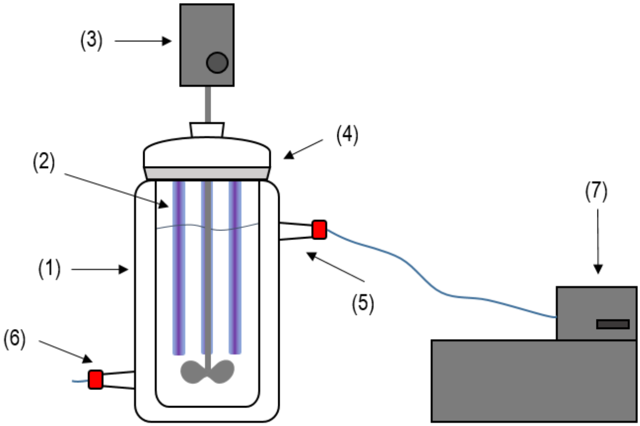


Figure 5. Reactor Device. (1) Jacketed reactor, (2) BLB lamps, (3) propeller agitator, (4) Aluminium foil, (5) Thermostatic bath (IN), (6) Thermostatic bath (OUT), (7) Thermostatic bath with temperature controller.

4.3. ANALYTICAL METHODS

4.3.1. High Performance Liquid Chromatography (HPLC)

After sample withdrawal from reactor, it was filtered them through 0.45 µm filters (for HPLC security). In this case, in addition, sample aliquots were immediately placed in vials containing methanol (1:1 mixure), in order to stop the reaction. SMX concentration was then analysed by an HPLC 1260 Infinity by Agilent Technologies. The chromatographic conditions were set as follows:

- Column: Mediterranea Sea 18 by Teknokroma, 250 x 4.6 mm and 5µm particle size)
- Injection volume: 20 µL.
- Temperature: 20ºC.
- The mobile phase was a water/acetonitrile mixture at a 2:3 volumetric ratio. (The water was Milli-Q® acidified to pH 3 with orthophosphoric acid.)
- Flow rate: 1 mL/min
- Detection wavelenght: 214.4 nm

4.3.2. Determination of iron species

It was used the 1,10-phenantroline colorimetric method according to the International Organization for Standardization 1988 (ISO6332) for Fe(II) determination. In this method, we related the concentration of ion Fe (II) to the absorbance of the red-coloured complex at 510 nm wavelength measured by Hach Lange DR 3900 spectrophotometer. The complex is formed with 1,0-phenanthroline and Fe (II), according to the followind reaction:

$$\text{Fe (II)} + 3\ \text{Phen} \rightarrow [\text{Fe(Phen)}_3]^{2+} \qquad \text{Eq 3.1}$$

After Fe (II) determination, Fe (III) in solution is reduced to Fe (II) with ascorbic acid, in order to determine total iron (Fe(II) plus Fe(III)). The difference between total iron and Fe (II) can be used to determinate Fe (III). [20]

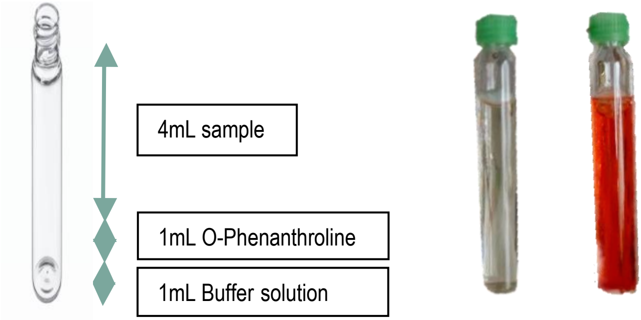


Figure 6. Example of analysis of iron without Fe(II) before/after add ascorbic acid.

4.3.3. Determination of hydrogen peroxide consumption

It was determinate hydrogen peroxide concentration by the metavanadate procedure employing a Hach Lange DR 3900 spectrophotometer in the colorimetric determination. In this case, the concentration is related to the absorbance of the orange-coloured oxovanadium(IV) at 450 nm. The equation 4.1 shows the reaction in which this method is based [21].

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow 3H_2O + VO_2^{3+} \qquad \text{Eq 4.1.}$$

The standards absorbance-concentration curves for iron and hydrogen peroxide are shown in appendix Figure 14 and 15.

4.3.4. Total Organic Carbon (TOC)

Total organic carbon (TOC) is a measure of the content of carbon from dissolved and undissolved organic substances in water. That is a standard analysis for water and wastewater characterization, which gives an idea about the degree of pollution of the aqueous sample. In AOPs research, this analysis is also useful to estimate the degree of mineralization (*i.e.*, transformation to CO_2 and H_2O, among other mineral species) of a sample initially containing a known mixture, as was the case of the present work.

The TOC analysis was done according to 5310B-standard method: High-Temperature Combustion Method (680ºC). It was performed with a Shimadzu 5055 TOC-VCSN analyser with an ASI-V Auto sampler [22].

The analysis for each oxidized sample was prepared just after withdrawal by adding a few drops of sodium bisulphite, in order to stop the reaction and do not interfere with the results.

5. RESULTS AND DISCUSSION

For the first experiments, we wanted to study under what conditions the Fenton process with zero valent iron presented the best performance. So we did a preliminary study on the reaction of Fenton with ZVI and its performance with the variation of the ratio ZVI / H_2O_2 and the pH, addition of other catalysts and its comparison with the use of WMS.

5.1. PRELIMINARY EXPERIMENTS

Table 6 shows the 28 experiments performed with the different operational conditions, as its was explained in section 4. It was varied pH, concentration and type of iron as a reagent with ZVI and WMS and other reagents like chloride and oxygen. The experiments are based on the combination of iron concentrations ranging from 0,5 to 5 g/L and peroxide ranging from 2 to 10 mmol/L with the pH variation from 2.8 to 5.5. The oxygen added in the experiments was at a pressure of 2 bar and was bubbled by means of porous steel diffusers with 10 µm pore size. For these preliminary experiments, three samples were taken at minutes 0, 50 and 90 to be able to observe in a general way the tendency of the reaction and make possible to decide which experiments should be done in the bench reactor.

Table 6. List and results of SMX degradation of all preliminary experiments at 90 minutes.

Experiment Nº	Conditions				Degradation of SMX (%) 90 min reaction
	pH	Fe (g/L)	H_2O_2 (mmol/L)	Others	
1a	5,5	0,5	2	-	2,9
2a				+ 10 ppm Cl^-	8,7
3a				+ O_2	0,0
4a			10	-	0,0
5a				+ 10 ppm Cl^-	0,0
6a				+ O_2	0,0
7a		5	2	-	0,4
8a				+ 10 ppm Cl^-	5,0

9a				+ O_2	0,0
10a			10	-	0,0
11a				+ 10 ppm Cl^-	2,1
12a				+ O_2	0,0
13a	2,8	0,5	2	-	**100,0**
14a				+ O_2	**100,0**
15a			10	-	**100,0**
16a				+ O_2	**100,0**
17a			0	-	22,4
18a		5	2	-	**100,0**
19a				+ O_2	**100,0**
20a			10	-	**100,0**
21a				+ O_2	**100,0**
22a			0	-	28,8
23a		0,5	2	-	**100,0**
24a			10	-	**100,0**
25a			0	-	6,0
26a		5	2	-	**100,0**
27a			10	-	**100,0**
28a			0	-	16,8

. In experiments from 13a to 27a except in those for which addition of hydrogen peroxide was not performed, more than 95% of degradation were observed already at 50 minutes of reaction. That is because pH clearly plays an important role in the Fenton oxidation process.

There was a little degradation in the experiments with pH 5. The most efficient condition showed about 8% SMX degradation, which coincides with the addition of chloride in the reaction. Apparently, in the presence of Cl^- the Fenton reaction contributed negligibly to the H_2O_2 decomposition. Chloride ions accelerated the decomposition of H_2O_2 by inducing pitting corrosion and accelerating the anodic dissolution of ZVI [25]. We see that it is necessary to acidify the reaction medium to those conditions in which we work to generate $HO\cdot$ radicals and achieve high oxidation rates. Numerous authors have studied the influence of this variable in the treatment of different industrial effluents, finding the optimum value of pH in 2.8 ± 0.2. [12][26][27]. This causes a disadvantage of the process since at higher pH iron tends to precipitate and generate sludge that must subsequently be filtered or sedimented to separate the waste, a part of the cost of acidify all the effluent and turn at the end of reaction again to circumneutral pH. (Figure 7)

Figure 7. Example of sludge generated by precipitated iron.

The influence of the ZVI / H_2O_2 ratio is not evident in these experiments. It seems that the more the concentration of iron the degradation would be better, or that there is a slight tendency that the Fenton reaction occurs more effectively with less H_2O_2 concentration.

In addition, it can be seen in experiment 17a, 22a, 25a, and 28a that oxygen plays an important role on Fenton reaction when using ZVI or MWS as catalysts. In those reactors, it can be degraded to almost the 28 % of SMX only with ZVI and oxygen bubbling (and without hydrogen peroxide addition). It can not be confirmed that in this qualitative type of experiments, there is a significant percentage of SMX can be degraded only with a good aeration in pH 3. This aeration oxygen seems sufficiently oxidizing to react with iron in low quantities, but does not reach the values to be considered good enough to be effective for degrade the pollution of water.

5.2. BENCH REACTOR

The principal objective is to study and test the use and effectiveness of iron as a “low cost” catalyst in advanced oxidation processes. In the table below, the experiments that were carried out in the main reactor (figure 5) are presented. It was studied the comparison of ZVI and WMS and the optimal ratio and its potential reusability. In these experiments, eight samples were taken from the reactor at 0, 1, 5, 15, 30, 45, 60, and 90 minutes. The water of all treatments was Milli-Q water, which being ultrapure, has a very small TOC value (2 ppb). Consequently only the presence of our contaminant exists in the water, accordingly the Fenton reaction degrades only the pollutant (SMX).

In previous experiments, the tendencies and possible variations due to alternative experimental conditions compared to the classic Fenton process were studied. Perform the process at a pH close to neutrality and acid and compare this degradation. The maximum admissible values in the effluents of iron diluted in water is 10 ppm [6]. Thus, that was the concentration initial of iron for respect the legislation in the experiments carried out in the bench reactor.

Table 7. List and results of SMX degradation of all experiments in the bench reactor at 90 minutes.

Experiment	**Conditions**					**Degradation of SMX (%)**
	pH	**Iron (ppm)**		**H_2O_2 (ppm)**	**Others**	
1b	3	ZVI	10	68	-	**100.0**
2b				340	-	**98.9**
3b	5			68	-	3.3
4b				340	-	1.1
5b	3	WMS	10	68	-	14.8
6b				340	-	9.3
7b			100	68	-	**99.7**
8b				340	-	**98.2**
9b			1000	68	-	**100.0**
10b				340	-	**100.0**
11b			100	340	First reuse	**100.0**
12b					Second reuse	**100.0**
13b				68	Photo Fenton process	**100.0**
14b				340		**100.0**
15b	5	WMS	100	68	-	16.5
16b				340	-	5.3
17b		ZVI	500	340	-	0.2
18b					+10 ppm Cl-	7.8

5.2.1. Comparison between ZVI and waste metal shavings

The following figure includes the results of six experiments in which the iron concentration is 10 ppm and it was varied pH 2.8 to 5.5 and peroxide ratio from 2 to 10 mmol/L (which is equal to 68 to 340 ppm H2O2). In addition, the use of waste metal shavings as catalyst was compared to zero valent iron.

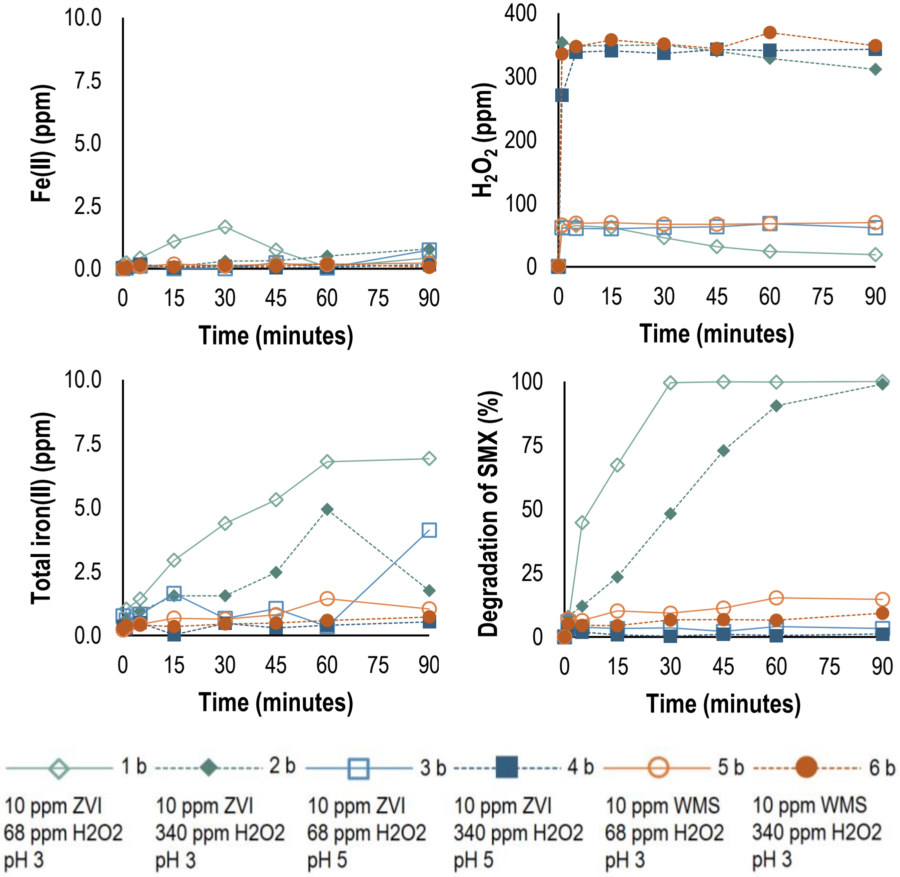


Figure 8. Graphics of results of concentration Fe(II), peroxide and percentage of degradation of SMX in 90 minutes of experiments 1b, 2b, 3b, 4b, 5b, and 6b.

As shown in Figure 8, practically there is no Fe (II) dissolved during the reaction except in experiment 1 and 2. Iron ions evolve during both Fenton reaction in such a way that zero valent iron, which acts as a catalyst, is initially consumed to form Fe (III) and HO · radicals according with

Eq.1.1 and Eq.1.2. It is observed how the total iron does not remains constant during the reaction, which indicates that the iron has precipitated during the process.

In turn, it can be seen how hydrogen peroxide is consumed throughout the experiment as it acts as a reactant in the Fenton process only in experiments 1 and 2.

For the others experiments, it seems that Fenton reactions do not occur significantly in spite of a small degradation results observed with acidic pH (less than 17%). Numerous authors have studied this process of advanced oxidation centred on Fenton, with all its possible variants, in which pH has a determining influence. It is necessary to perform the reaction at acidic pH to active iron species (II) as a catalyst for the decomposition of peroxide into radicals and achieve high oxidation rates. The Fe(II) in Fenton reaction presents its maximum catalytic activity at pH 2.8. An increase or decrease in this value sharply reduces the efficiency of the process. With basic pH, the Fe(III) precipitates as $Fe(OH)_3$ and at lower values of pH the reaction of generation of Fe(II) from Fe(III) is inhibited [12].

The pronounced effect of the initial pH of the process is related to the state in which iron is found, which, in turn, influences the formation of hydroxyl radicals according to equations 1.1 and 1.2 [28]:

$$Fe(II) + H_2O_2 \rightarrow Fe(II) + HO\cdot + OH^- \quad k: 76\ L/(m\ s) \qquad Eq.\ 1.1$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2 + H^+ \quad k: 0.01\ L/(m\ s) \qquad Eq.\ 1.2$$

An obvious point in this comparison is that the waste metal shavings do not release the same amount of dissolved iron as the ZVI. As shown in figure 8, ZVI works better than WMS at the same conditions. Several explanations can be found for these results. It is possible that there is some residue in the surface of WMS, despite the previous cleaning, that could hinder the contact of iron with the aqueous medium. It could also be that the relatively big size or particular shape of iron particles hinders its dissolution because of a low contact area. The iron shavings, after a gridding and sintering treatment, could make possible a higher diffusion or dissolution of the iron in water.

5.2.2. Optimal ratio for waste metal shavings

The ratio chosen in previous experiments was 10 ppm of iron as fixed by the legislation of maximum admissible values in the effluents, and 68 or 340 ppm of H_2O_2. As it was shown in the previous section, that concentration of iron is not enough to make possible the reaction so the next four experiments were performed with 100 and 1000 ppm of iron as WMS, also with concentrations of 68 and 340 ppm of H_2O_2. (Figure 9)

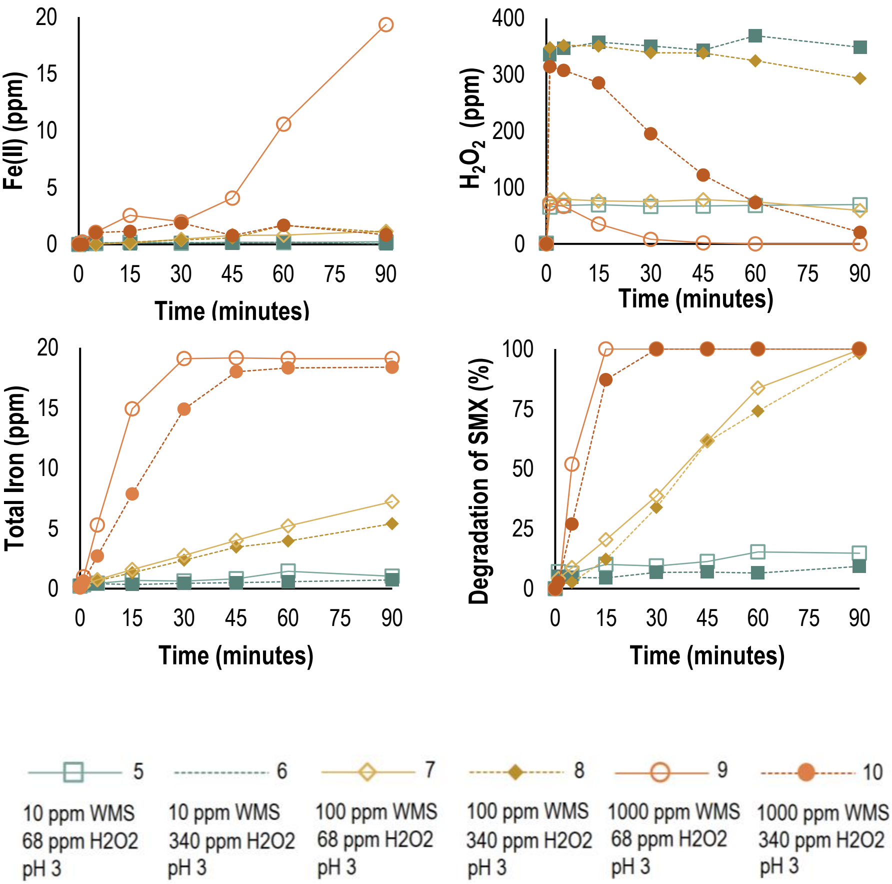


Figure 9. Graphics of results of concentration Fe(II), peroxide and percentage of degradation of SMX in 90 minutes of experiments 5, 6, 7, 8, 9 and 10.

As shown in Figure 9, iron ions evolve during the Fenton reaction in such a way that Fe (II), which acts as a catalyst, is consumed to form Fe (III) and radicals HO· quite better in experiments 9 and 10 than experiments 7 and 8. In a group of three its compare in scale of 10 ratios of iron and peroxide: green 10 ppm, yellow 100 ppm and orange 1000 ppm WMS. It is observed that as it increase the concentration of WMS, the iron that is in solution increases and peroxide decreases, therefore Fenton reaction occurs more easily (speed) and the complete degradation of SMX occurs in less time. It could be said that is better to work with the highest concentration of iron (*i.e.*, experiments using 1000ppm WMS / 68-340 ppm H_2O_2, represented by orange series in Figure 9). However, we must not exceed the legal limit of 10 ppm of iron in solution, so the optimum range to work would be between 1000 and 100 ppm of waste metal shaving. Probably, for according to these legal requirements, it would be more recommendable working with 100 ppm of WMS.

In turn, it can be seen how hydrogen peroxide is consumed throughout the experiment as it acts as a reactant in the Fenton process better in experiments with low concentration (68 ppm H_2O_2). An excess of peroxide produces more hydroxyl radicals or generates more Fe(II) (Eq 1.1 and 1.2). A high concentration of peroxide and radicals $HO\cdot$ increases the speed of reactions that increase his own disappearance according to the following reactions[29][30]:

$$H_2O_2 + HO\cdot \longrightarrow HO_2\cdot + H_2O \qquad k=2.7\cdot10^{7}\ L/(m\cdot s) \qquad \text{Eq. 5.1}$$

$$HO_2\cdot + HO\cdot \longrightarrow O_2 + H_2O \qquad k=1\cdot10^{10}\ L/(m\cdot s) \qquad \text{Eq. 5.2}$$

$$HO\cdot + HO\cdot \longrightarrow H_2O_2 \qquad \text{Eq. 5.3}$$

Also, the effect of the ions that are present in the water matrix influences the reaction so that the scavenger effect can happen. The scavenging effect refers to the ability of many antioxidants to act as stabilizers or inhibitors of various reactive species. In the case of free radicals, such action implies its stabilization through the assignment of an electron to these reactive molecules, so that there is an inhibition of degradation rate of the target pollutant due to of the disappearance of hydroxyl radicals. Therefore, the higher the concentration of these ions (with 340 ppm H_2O_2), the higher the scavenging effect of the hydroxyl radicals and the lower the degradation observed [31][32].

On the other hand, the residual concentration of hydrogen peroxide that remains in the medium after the treatment contributes to toxicity, which forces to conveniently adjust the rate used, so that the treated effluent does not exceed the limits of established discharges. Probably for security would be recommendable to work with 68 ppm of H_2O_2.

By increasing either ZVI or H_2O_2 the reaction rate and therefore the efficiency of the degradation of pollutant decreases. It is desirable that the ratio of H_2O_2 to ZVI should be as small as possible.

5.2.3. Reuse of waste metal shavings

As experiment 9 was the one exhibiting one of the best performances (high degradation in less time), that scenario was selected to study the reusability of WMS as catalysts. As in the rest of experiments, dissolved iron (II) and total iron, hydrogen peroxide, degradation of sulfamethoxazole and TOC were analysed. Figure 10 shows experiments 9, 11 and 12 with the option to reuse of iron.

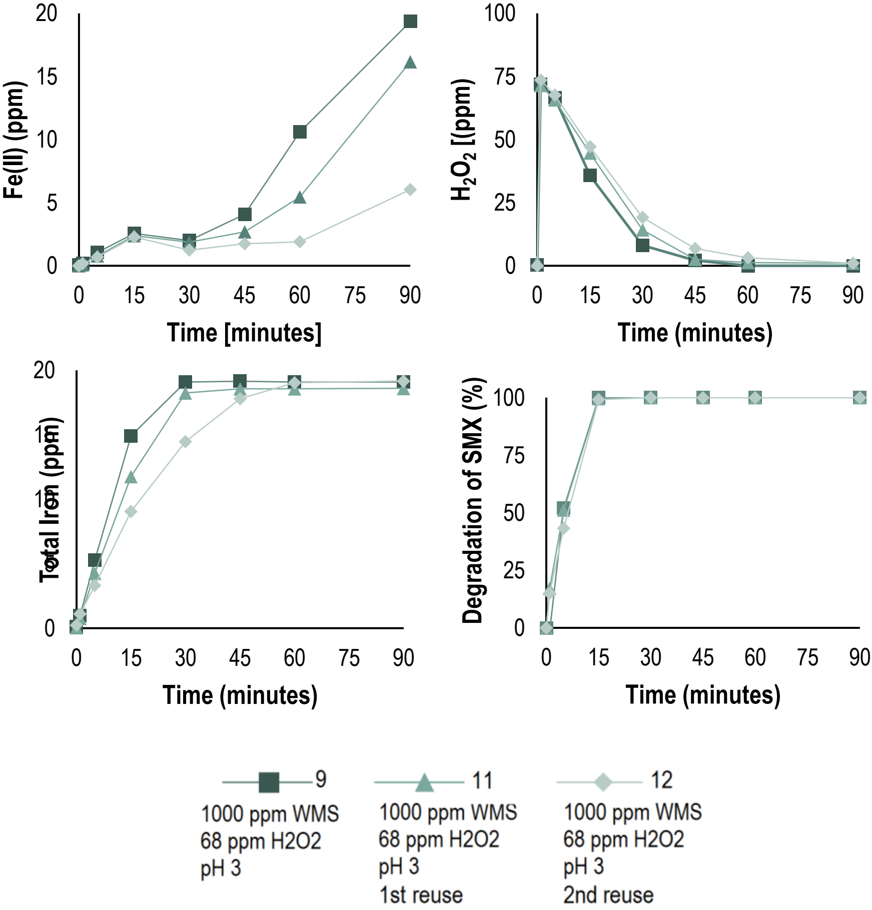


Figura 10. Graphics of results of concentration Fe(II), peroxide and percentage of degradation of SMX in 90 minutes of experiments 9, 11 and 12.

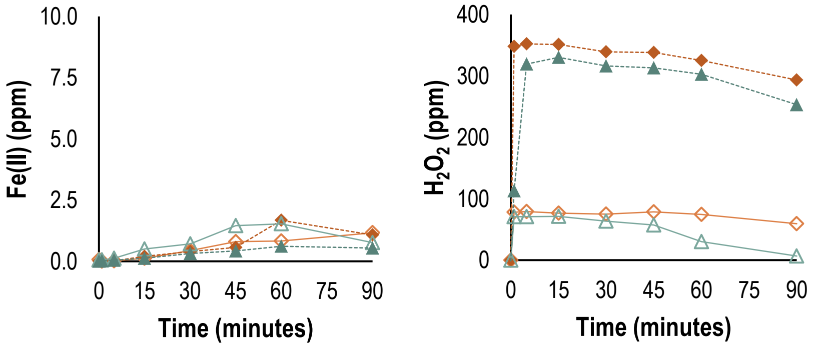
It can be observed a slight tendency to lose its oxidizing properties as we filter and reuse the iron. Even so, as regards the degradation of SMX, there are practically no differences. The complete degradation occurs between 15 and 30 minutes of reaction. Moreover, it is observed that both iron and peroxide are generated and consumed respectively in a very similar way between the three experiments. So, It can be confirmed that the reuse of the iron shavings is a good option to operate considering that generate less waste and reduce material expenses.

One of the advantages that it can be obtained from WMS is that it can be reused them at least three consecutive times without appreciating many differences in the degradation of our contaminant. In addition, we can recover it by sedimentation or filtration. This is in contrast with the original Fenton, in which iron must be again introduced. [11][12]

5.2.4. Photo-Fenton-like vs Dark-Fenton-like

One of the possible improvements for Fenton reaction is to apply ultraviolet radiation to promote the reductive regeneration of Fe (II) (see section 1.4.1). This AOP is based on principles that are common to Fenton making use of a catalyst like Fe (II) ion but with simultaneous use of ultraviolet/visible radiation. Therefore, the photo-Fenton process is faster than dark Fenton and also allows the generation of HO·. [12][23]

To make the comparison it was chosen experiments 7 and 8 since the degradation of SMX was not complete and it could be observed there was Fe (III) in solution available for *UV* to generate Fe (II) and improve the process. For Photo-Fenton process, three mercury lamps (low-pressure) BLB Philips TL 8W-08 FAM with 8W electric power were employed. The BLB radiation range was from 300 nm to 410 nm, having the maximum peak of light emission at 365 nm. Figure 11 shows experiments 7, 8, 13, and 14 following the same patterns as before.



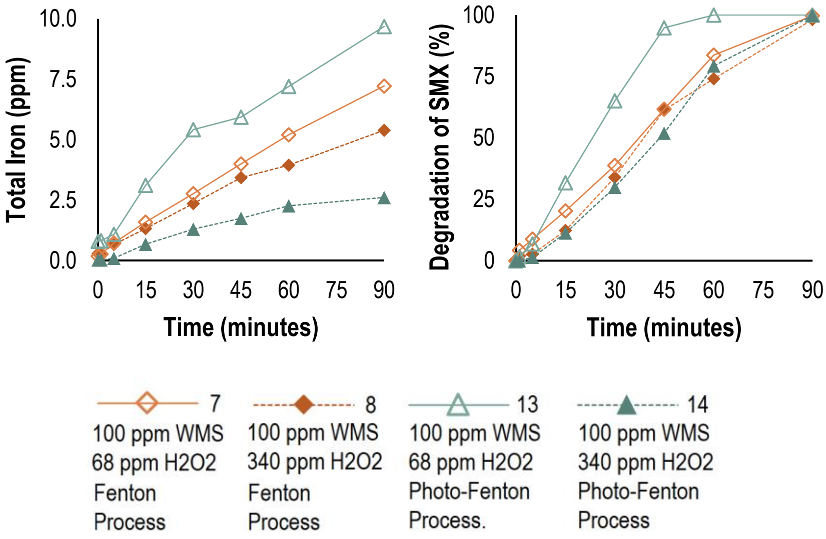


Figure 11. Graphics of results of concentration Fe(II), peroxide and percentage of degradation of SMX in 90 minutes of experiments 7, 8, 13 and 14

It can be observed in figure 11, as in the previous cases, that experiments with a higher concentration of peroxide impair the efficiency of the degradation and dissolution of iron. It can be seen that with the use of UV radiation there is a significant improvement in the process about 30% faster than dark Fenton. It would be necessary to verify if economically we would be interested or the cost of electricity that it supposes would not benefit us enough in terms of the degradation of the pollutant.

It is interesting to observe how effectively the peroxide concentration is key to increase or decrease the efficiency of our process. Over again, it is recommendable to work with lower concentrations of it to avoid inhibitions in the reactions of the process.

5.2.5. Mineralization of pollutant

Total organic carbon (TOC) is a measure for the content of carbon from dissolved and undissolved organic substances in water. It is one of the most important composite parameters in the assessment of the organic pollution of water. This also estimate the degree of mineralization. The theoretical TOC for the solution that contains Sulfamethoxazole is 9.49 mg/L.

Figure 12 shows the mineralization of experiments with a degradation of SMX higher than 98%.

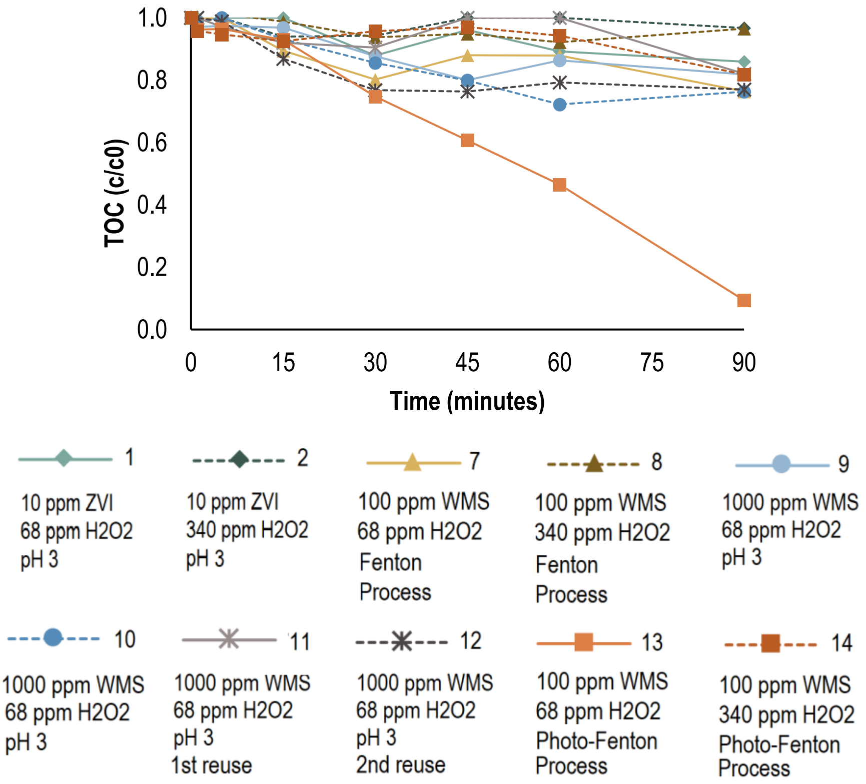


Figure 12. Graphic of results of TOC (c/c$_0$) in 90 minutes of experiments 1, 2, 7, 8, 9, 10, 11, 12, 13 and 14.

As shown in figure 12, except experiments 2 and 8 (which were performed with 340 ppm of peroxide), the mineralization of the pollutant was between 20 and 30 percent. The best and the only experiment with an almost complete mineralization was the experiment 13. This can be expected since it worked with the optimal MWS/peroxide ration and it is light assisted.

5.2.6. Kinetics of SMX

The degradation reaction of SMX were fitted to pseudo first order kinetics using following equation:

$$C_{SMX}=C_{SMX,0}\cdot\exp(-k\cdot t)$$

Linearizing it (Figure 13**)** the value of the kinetic constant, *k*, can be obtained from the slope of the linearization. The *k* values obtained, with their corresponding R^2 values, are shown in Table 8. For the replicated experiments the average and the standard deviation were calculated.

These kinetics constants were calculated for experiments with a degradation > 98% since for the other reactions with such a low percentage the reaction rate could not be accurately determined.

The k value was calculated for each experiment assuming reaction orders of 0, 1, and 2 with respect to SMX concentration. The model that better described the abatement process was the one corresponding to pseudofirst-order kinetics.

Table 8. Kinetics results for each experiments (with more than 90% of SMX degradation)

Experiment	Conditions		K (min^{-1})
	rate Fe / H2O2	Others	
1	10 /68	ZVI	0.119
2	10 /340	ZVI	0.047
7	100 /68	WMS	0.055
8	100 /340	WMS	0.039
9	1000 /68	WMS	0.418
10	1000 /340	WMS	0.141
11	1000 /68	WMS 1st reuse	0.373
12	1000 /68	WMS 2nd reuse	0.317
13	100 /68	WMS Photo-Fenton	0.061
14	100 /340	WMS Photo-Fenton	0.058

According to the obtained results, the highest kinetic constant was observed for experiment 9, followed by experiments 11 and 12, which correspond to WMS reuse experiments. In general the reaction rates increased when more iron or less peroxide were used in the process. Also it can be seen that Photo-Fenton is faster than Fenton-Like (Experiment 13/14 vs Experiment 7/8), although in any case the treatment worked better with less peroxide or a higher Fe(II)/H_2O_2 ratio. By the same token, for a study of kinetics, we should test more experiments.

5.2.7. Economical consideration

An economical assessment was performed taking into account different experimental conditions used in the oxidation processes tested in this work. The calculation was based in the work published by Bolton to normalize the efficiency of the AOPs (Bolton et al. 2001). Thus, the electrical energy per order of magnitude (EEO) was calculated taking into account electricity costs of irradiation, mixing and chemical costs, all of them normalized to the reactor volume (Bolton et al. 2001). It was only considered operational cost and not capital or maintenance cost. I was not considered also any product for analysis. All dates of product price were taken for chemical reagents used of technical-scale commercial price and energy values are from Eurostat. [33]

For comparison of economical requirements of the different experiments, only experiments with significantly high degradation and both rates of H_2O_2. Experiments 1, 2 and 7, 8, 9 were chosen to compare ZVI and WMS. Experiment 7 and 13 were chosen to assess the necessity of implementing Photo-Fenton process. Experiments 11 and 12, on their part, were selected to take into account the reuse of the waste metal shavings.

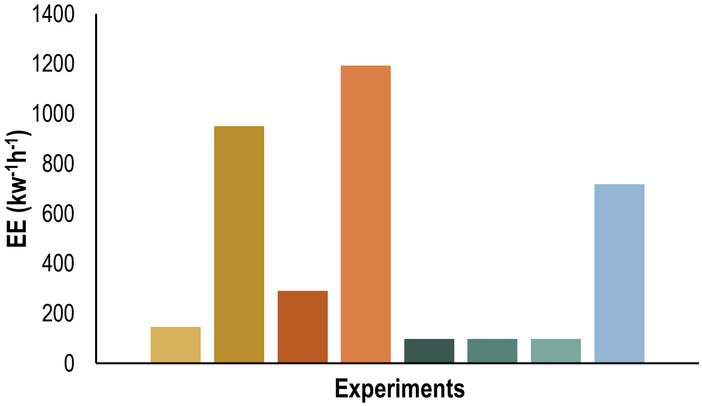
For the estimation of the Energetic Efficiency (EE) in ppm $\cdot kW^{-1} \cdot h^{-1}$, the following equation has been used:

$$EE= (C_{PROP,o} - C_{PROP})/(P \cdot t)$$

P: nominal power (kW)

$C_{PROP,o}$: initial concentration (ppm)

C_{PROP}: final concentration (ppm)



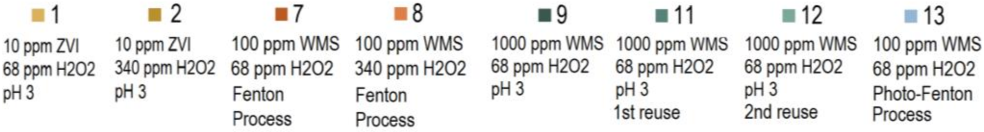


Figure 13. Efficiency results for experiment 1, 2, 7, 8, 9, 11, 12, and 13.

In this graphic, it is shown that using an excess of peroxide does not benefit the efficiency of the reaction, and also that it is better to use WMS than ZVI. Regarding the use of light, it can be said that for the energetic efficiency of the degradation of SMX the use of light to regenerate the catalysis is no required. However, further research should be carried out to improve the treatment.

The operating conditions with the highest cost-performance ratio is a Fenton process with 1000 / 68 of WMS / H_2O_2 and with its reuses. But, it has to be taken into account that the experiment 13 was the only one with a complete mineralization of the pollutant.

6. CONCLUSIONS

- Fenton oxidation as a combination of waste metal shavings with H_2O_2 at acid pH to generate hydroxyl radicals is an alternative or a complementary solution to conventional wastewater treatment processes for industrial wastewater treatment. An advantage the waste metal shaving can be used over without requiring regeneration or replacement and can be removed from the treated water by sedimentation or filtration.
- The use of an H_2O_2 concentration higher than the presumed amount depending on the origin of the iron does not improve the elimination of the organic material in the Fenton process. Although this excess generates $HO\cdot$ or Fe (II) radicals, it acts in reactions that imply the disappearance of them or by a scavenger effect.
- It is advisable to work with rate 100 / 68 of WMS / H_2O_2 for to not exceed the allowable limit and obtain 100% of SMX degradation. In this case it is not require incise radiation. In turn of a complete mineralization, the rate to work is 1000 / 68 of WMS / H_2O_2 with incise radiation.
- Another advantage of using WMS as an agent in a Fenton reaction is the high effectiveness in reusing it.
- There are recent works that say that the ZVI-H_2O_2 process works well degrading organic pollutants, the replicas of those experiments that have been done in this work, in spite of having carried out them with the same experimental conditions, indicate completely the opposite.

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ACRONYMS

AOPs	Advanced Oxidation Process
BLB	Black Light Bulbs
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
ECs	Emerging Contaminants
EU	European Union
Fe^{+2}	Iron (II), Fe (II)
Fe^{+3}	Iron (III), Fe (III)
HPLC	High Pressure Liquid Chromatography
H2O2	Hydrogen Peroxide
H2SO4	Sulphuric acid
NCA	Normativas Control Ambiental
HO·	Hydroxyl radicals
POA	Procesos de Oxidación Avanzada
ppm	Part per million [mg/L]
SCWO	Supercritical Water Oxidation
SMX	Sulfamethoxazole
TOC	Total Organic Carbon
UV	Ultraviolet radiation
WAO	Wet Air Oxidation
WWTP	Waste Water Treatment Plant

APPENDICES

APPENDIX 1: RESULTS OF SMX DEGRADATION, IRON, HYDROGEN PEROXIDE AND TOC FOR EACH EXPERIMENT.

The results of degradation SMX, the concentration of all the iron species and hydrogen peroxide and TOC. All the experiments were carried out at bench reactor at 20ºC with a initial concentration of SMX 20 ± 2 ppm.

***Table 9**. Experiment 1b results. Ratio 10 / 68 (ZVI / H_2O_2) pH3*

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0.00	0.17	0.15	0.33	1.7	1,00
1	5.04	0.23	0.79	1.02	61.0	1,04
5	44.,81	0.44	0.98	1.42	64.9	1,06
15	67.32	1.10	1.85	2.94	62.1	1,08
30	99.48	1.66	2.72	4.38	45.9	0,88
45	99.84	0.74	4.56	5.30	31.9	0,96
60	99.77	0.07	6.72	6.79	24.0	0,89
90	100.00	0.44	6.47	6.91	19.3	0,86

Table 10. Experiment 2b results. Ratio 10 / 340 (ZVI / H_2O_2) pH3.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,04	0,28	0,32	0,5	1,00
1	8,06	0,04	0,58	0,62	353,8	0,99
5	12,02	0,08	0,85	0,94	348,0	1,01
15	23,44	0,30	1,24	1,55	348,9	0,94
30	48,26	0,31	1,23	1,54	349,7	0,94

45	72,91	0,51	1,96	2,46	340,2	1,09
60	90,42	0,79	4,13	4,92	328,5	1,03
90	98,94	0,63	1,12	1,75	311,2	0,97

Table 11. Experiment 3b results. Ratio 10 / 68 (ZVI / H_2O_2) pH5.

Time (min)	**Degradation (%)**	**Fe (II) (ppm)**	**Fe (III) (ppm)**	**Total Iron (ppm)**	**H_2O_2 (ppm)**	**TOC (c/c_0)**
0	0,00	0,00	0,76	0,77	0,3	1,00
1	5,99	0,03	0,57	0,60	61,7	1,06
5	3,78	0,12	0,70	0,82	60,6	1,03
15	3,31	0,00	1,63	1,63	59,7	1,01
30	3,57	0,01	0,64	0,65	62,1	1,03
45	2,17	0,24	0,81	1,05	62,7	1,00
60	4,11	0,04	0,31	0,35	67,8	0,99
90	3,33	0,74	3,38	4,12	61,4	1,00

Table 12. Experiment 4b results. Ratio 10 / 340 (ZVI / H_2O_2) pH5.

Time (min)	**Degradation (%)**	**Fe (II) (ppm)**	**Fe (III) (ppm)**	**Total Iron (ppm)**	**H_2O_2 (ppm)**	**TOC (c/c_0)**
0	0,00	0,04	0,31	0,35	0,0	1,00
1	2,45	0,06	0,20	0,26	270,4	1,11
5	1,89	0,17	0,32	0,49	338,5	1,07
15	0,82	0,04	0,02	0,03	340,6	1,03
30	0,29	0,10	0,38	0,48	336,3	1,00
45	1,00	0,04	0,26	0,30	342,5	1,08
60	0,59	0,06	0,34	0,40	341,0	1,04
90	1,13	0,16	0,37	0,53	342,9	1,06

Table 13. Experiment 5 results. Ratio 10 / 68 (waste metal shavings / H_2O_2) pH3.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,21	0,00	0,20	1,7	1,00
1	7,02	0,08	0,22	0,30	65,5	0,96
5	6,40	0,08	0,35	0,43	68,5	1,03
15	10,16	0,19	0,48	0,67	69,5	0,94
30	9,37	0,12	0,51	0,63	66,8	0,97
45	11,29	0,19	0,62	0,81	67,0	0,94
60	15,31	0,17	1,26	1,44	68,3	0,94
90	14,76	0,23	0,81	1,03	69,7	0,95

Table 14. Experiment 6b results. Ratio 10 / 340 (waste metal shavings / H_2O_2) pH3.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,02	0,25	0,27	0,8	1,00
1	5,16	0,02	0,37	0,39	335,5	1,00
5	4,59	0,15	0,25	0,41	347,0	1,10
15	4,43	0,08	0,26	0,34	357,8	1,01
30	6,75	0,15	0,30	0,45	350,8	1,03
45	6,85	0,10	0,38	0,48	343,8	1,02
60	6,55	0,19	0,39	0,58	369,1	1,02
90	9,29	0,06	0,66	0,72	348,5	1,01

Table 15. Experiment 7b results. Ratio 100 / 68 (waste metal shavings / H_2O_2) pH3.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,00	0,18	0,29	0,0	1,00
1	4,22	0,00	0,26	0,30	77,8	0,92
5	8,82	0,02	0,71	0,65	79,1	1,06

15	20,33	0,20	1,39	1,32	76,3	0,89
30	38,72	0,40	2,37	2,36	75,1	0,80
45	61,65	0,56	3,44	3,43	78,5	0,98
60	83,70	1,67	3,54	3,95	74,4	0,88
90	99,70	1,08	6,15	5,39	59,5	0,76

Table 16. Experiment 8b results. Ratio 100 / 340 (waste metal shavings / H_2O_2) pH3.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,06	0,23	0,18	0,0	1,00
1	1,92	0,01	0,30	0,26	348,3	1,16
5	2,68	0,01	0,64	0,73	352,1	1,01
15	12,28	0,12	1,20	1,59	351,0	0,99
30	33,93	0,44	1,92	2,77	339,1	0,94
45	61,25	0,80	2,64	4,00	338,3	0,95
60	74,05	0,82	3,13	5,21	325,1	0,92
90	98,15	1,16	4,23	7,22	293,4	0,97

Table 17. Experiment 9b results. Ratio 1000 / 68 (waste metal shavings / H_2O_2) pH3.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,06	0,08	0,14	0,2	1,00
1	1,62	0,21	0,77	0,98	71,9	0,93
5	51,90	1,06	4,22	5,28	66,6	0,97
15	100,00	2,55	12,36	14,92	35,7	0,97
30	100,00	1,99	17,09	19,08	8,0	0,88
45	100,00	4,08	15,07	19,15	2,1	0,69
60	100,00	10,59	8,50	19,09	0,0	0,86
90	100,00	19,35	-0,27	19,08	0,0	0,82

Table 18. Experiment 10b results. Ratio 1000 / 340 (waste metal shavings / H_2O_2) pH3.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,00	0,05	0,05	0,0	1,00
1	2,65	0,00	0,62	0,62	314,4	0,99
5	26,92	1,05	1,64	2,69	307,8	1,02
15	87,17	1,14	6,73	7,86	285,7	0,93
30	100,00	1,89	13,01	14,90	195,7	0,86
45	100,00	0,77	17,24	18,01	122,5	0,80
60	100,00	1,70	16,61	18,31	73,4	0,72
90	100,00	0,83	17,55	18,38	20,8	0,76

Table 19. Experiment 11b results. Ratio 100 / 68 (waste metal shavings / H_2O_2) pH3. With First reuse.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,00	0,04	0,04	1,7	1,00
1	17,07	0,06	0,70	0,76	71,4	1,07
5	51,19	0,78	3,49	4,27	65,7	0,97
15	99,59	2,37	9,39	11,77	44,6	0,92
30	100,00	1,88	16,36	18,24	14,2	0,90
45	100,00	2,68	15,88	18,56	2,5	1,05
60	100,00	5,44	13,13	18,57	1,2	1,04
90	100,00	16,16	2,45	18,60	1,0	0,82

Table 20. Experiment 12 results. Ratio 100 / 68 (waste metal shavings / H_2O_2) pH3. With second reuse.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,00	0,24	0,24	0,0	1,00

1	14,99	0,16	0,94	1,10	73,6	1,07
5	43,16	0,69	2,64	3,32	67,6	0,99
15	99,06	2,27	6,79	9,07	47,2	0,87
30	100,00	1,23	13,23	14,46	19,1	0,77
45	100,00	1,74	16,05	17,79	6,8	0,76
60	100,00	1,89	17,15	19,05	3,1	0,79
90	100,00	6,04	13,13	19,16	1,0	0,77

Table 21. Experiment 13b results. Ratio 100 / 68 (waste metal shavings / H_2O_2) pH3. Photo-Fenton Process.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0	0,00	0,06	0,74	0,80	-
1	1	1,62	0,06	0,77	0,82	
5	5	6,91	0,12	0,96	1,09	
15	15	31,77	0,50	2,61	3,11	
30	30	65,02	0,71	4,71	5,42	
45	45	94,72	1,45	4,48	5,93	
60	60	100,00	1,53	5,67	7,20	
90	90	100,00	0,76	8,93	9,69	

Table 22. Experiment 14b results. Ratio 100 / 68 (waste metal shavings / H_2O_2) pH3. Photo-Fenton Process.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0	0,00	0,01	0,02	0,03	
1	1	0,00	0,02	0,00	0,02	
5	5	1,36	0,04	0,05	0,09	
15	15	11,28	0,12	0,56	0,67	
30	30	29,97	0,31	0,99	1,30	

45	45	51,87	0,42	1,32	1,75	
60	60	79,30	0,61	1,65	2,27	
90	90	99,81	0,54	2,07	2,61	

Table 23. Experiment 15b results. Ratio 100 / 68 (waste metal shavings / H_2O_2) pH5.

Time (min)	**Degradation (%)**	**Fe (II) (ppm)**	**Fe (III) (ppm)**	**Total Iron (ppm)**	**H_2O_2 (ppm)**	**TOC (c/c_0)**
0	0,00	0,00	0,00	0,00	0,2	
1	8,85	0,00	0,01	0,01	66,3	
5	10,23	0,03	0,01	0,04	68,7	
15	11,90	0,02	0,04	0,06	72,7	
30	13,94	0,04	0,01	0,05	71,7	
45	13,55	0,11	2,69	2,80	73,8	
60	14,31	0,04	0,31	0,35	73,1	
90	16,51	0,08	0,21	0,29	68,0	

Table 24. Experiment 16b results. Ratio 100 / 340 (waste metal shavings / H_2O_2) pH5.

Time (min)	**Degradation (%)**	**Fe (II) (ppm)**	**Fe (III) (ppm)**	**Total Iron (ppm)**	**H_2O_2 (ppm)**	**TOC (c/c_0)**
0	0,00	0,03	0,00	0,03	0,4	
1	2,38	0,01	0,18	0,19	350,6	
5	2,65	0,01	0,26	0,27	351,2	
15	3,88	0,02	0,30	0,32	357,6	
30	3,01	0,04	0,17	0,21	346,1	
45	5,01	0,04	0,17	0,21	346,1	
60	3,54	0,05	0,16	0,21	351,0	
90	5,31	0,06	0,33	0,39	226,1	

Table 25. Experiment 17b results. Ratio 500 / 340 (ZVI / H_2O_2) pH5.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,03	0,01	0,04	0,00	-
5	0,47	0,03	0,00	0,03	329,11	-
15	1,31	0,02	0,05	0,07	307,19	-
25	1,16	0,03	0,03	0,06	290,17	-
30	0,44	0,05	-0,01	0,04	280,60	-
40	0,82	0,06	0,02	0,08	265,91	-
50	-1,50	0,06	0,07	0,14	250,81	-
60	0,01	0,02	0,01	0,03	238,89	-

Table 26. Experiment 18b results. Ratio 500 / 340 (ZVI / H_2O_2) pH5 + 10 ppm chloride.

Time (min)	Degradation (%)	Fe (II) (ppm)	Fe (III) (ppm)	Total Iron (ppm)	H_2O_2 (ppm)	TOC (c/c_0)
0	0,00	0,00	0,40	0,40	0,00	-
10	1,22	0,04	0,07	0,11	319,53	-
30	-1,77	0,01	0,22	0,23	311,87	-
45	3,47	0,06	0,10	0,16	257,40	-
50	2,35	0,08	0,15	0,24	252,09	-
60	1,91	0,06	0,03	0,09	222,94	-
90	7,77	0,15	0,03	0,18	185,28	-
0	0,00	0,00	0,40	0,40	0,00	-

APPENDIX 2: THE STANDARD CALIBRATION-CONCENTRATION CURVE.

The graphs represent bellow are the standard calibration-concentration curve of the calibration made in the DR 3900 spectrum for iron and hydrogen peroxide and in HPLC.

Standard calibration for Iron

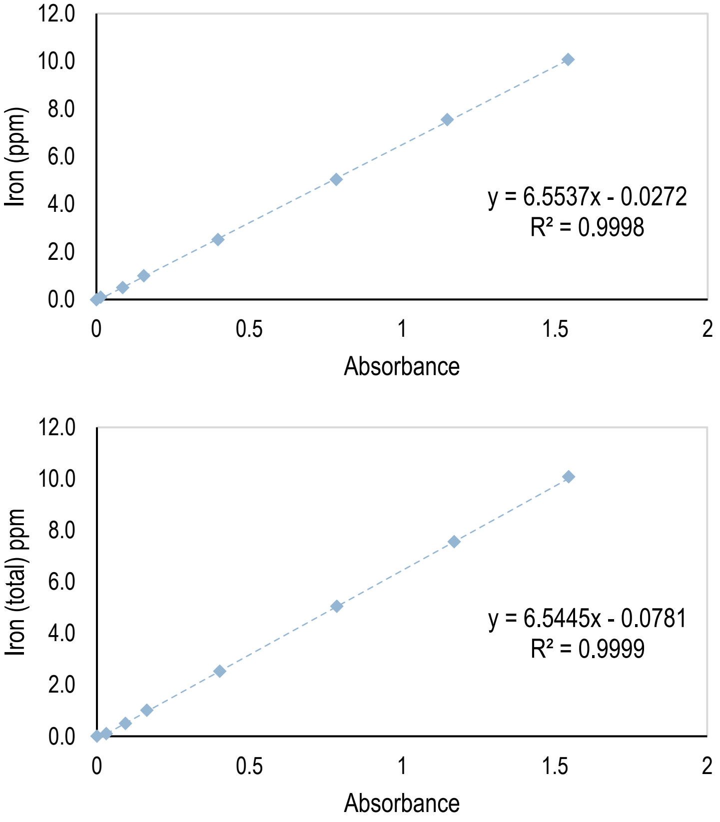

Figure 14. The standard calibration for Iron and Iron + Asr ac. at 510 nm on DR3900.

Standard calibration for peroxide hydrogen

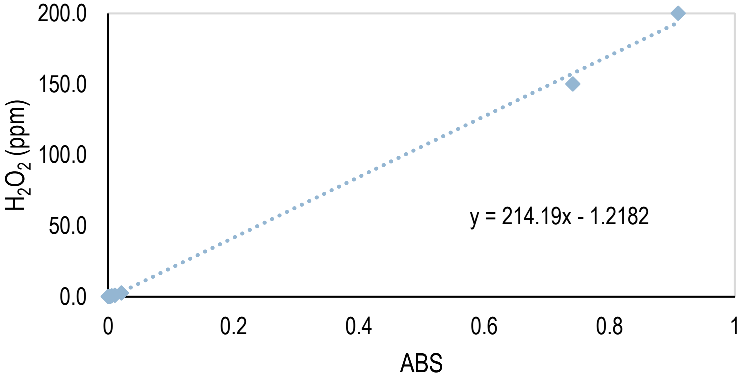

Figure 15. The standard calibration for peroxide hydrogen at 450 nm on DR3900.

Standard calibration for sulfamethaxole

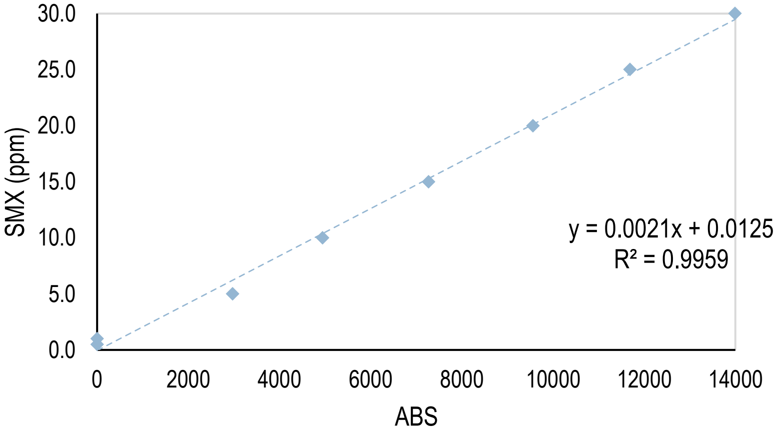

Figure 16. The standard calibration for Sulfamethoxazole on HPLC.