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Application of the photo-Fenton process at circumneutral pH to agricultural water reuse

Author

Claudia Lai

Director/s

Dr. Alberto Cruz Alcalde

Department of Chemical Engineering and
Analytical Chemistry,

University of Barcelona

Dr. Carme Sans Mazón

Department of Chemical Engineering and
Analytical Chemistry,
University of Barcelona

A mi familia

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Abstract

The high water consumption in agriculture (60-70% of freshwater) and the prediction of a significant growth usage led the scientific community to the concept that the reuse of WW is necessary. Advanced Oxidation Processes (AOPs) and, in particular, photo-Fenton technique showed up to be very useful for the elimination of micropollutants (MPs) and disinfection from wastewater by generating powerful Reactive Oxygen Species (ROS).

The strategy of this project consisted in involving three organic fertilizers (EDTA-Fe, EDDS-Fe and DTPA-Fe) in the application of the photo-Fenton process at neutral pH for Sulfamethoxazole (SMX) abatement (100%, 94.1% and 90.1% of SMX degradation, respectively). To be iron chelate agents, their employment permitted to avoid iron precipitation making plausible water reuse for agricultural purposes containing already a fertilizer. In this way, DTPA-Fe complex has been deeply investigated since it is the less known in scientific community so far, showing a great outcome in photo-Fenton technique application.

This thesis is focus on reaction’s mechanism of the process as there would be a chance that iron complexes would participate with dissolved oxygen and sunlight to the generation of ROS, which could have significant environmental implications if they are also formed in aquatic ecosystems.

From test with tert butanol as radical hydroxyl (HO·) scavenger, this most oxidation species showed up to be the responsible of SMX degradation. Also, the introduction of solar light in the system revealed a possible iron complex excitation and radical species formation ($[\mathrm{DTPA\text{-}Fe(II)}]^{*2-}$, $\mathrm{DTPA}\cdot^{3-}$, $\mathrm{O_2}\cdot^{-}$) so its engagement in reaction but at very minimum level. In addition, oxygen and hydrogen peroxide allowed the development of ROS species so increasing the efficiency of the process itself (69.2% when only H_2O_2 applied, 30.1% when only O_2 applied).

To sum up, photo-Fenton with iron complexes at neutral pH revealed to be very efficient technique in terms of reference compound removal, considering to be a possible strategy to apply in one line of WWTP (Wastewater Treatment Plant) to wastewater reuse in agriculture since the availability of solar light is free.

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1. INTRODUCTION

1.1 Current situation of water resources and “water stress” concept

Water is life, in all forms and shapes (The world water council, 2000).

Water is one of the most important resources on earth, without it there would be no life. Total Earth’s volume of water is about 1.400 billion km^3, 97% of this is seawater and only 2.5% is fresh water (Figure 1). This freshwater is storage in glaciers and ice caps (68.9%), while the remaining part is groundwater (30.1%) and surface.

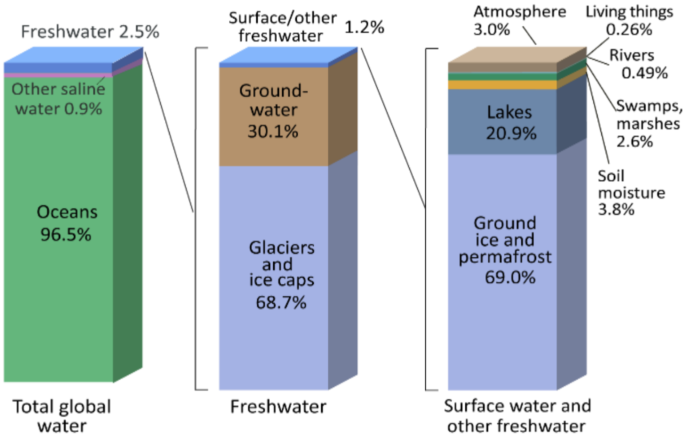


Figure 1.1. Water distribution on Earth. Source: Igor Shiklomanov’s chapter “World freshwater resources” in Peter H. Gleick (Editor), 1993, Water in Crisis: A Guide to the World’s Fresh Water Resources

Freshwater resources are renewed over the globe by the cycle of water, a continuous cycle of evaporation, precipitation and runoff [2] being heavily modified by climate change [3]. This, together with a growing world population and industrial expansion is leading to a lack of sufficient available water resources to meet water demand [4]. Water scarcity is one of the largest global risks which now affect more than 2.8 billion people in 48 countries and it is estimated to reach almost 7 billion by 2025 [5]. Stress levels will continue to increase as demand for water grows from 20 to 30% above the current level of use by 2050 [6]. In particular, agriculture sector counts the largest user overall in term of water consumption and withdrawal (about 69% of annual water withdrawals globally) [7].

1.2 Enhanced wastewater treatment and water reuse

"There is a water crisis today. But the crisis is not about having too little water to satisfy our needs. It is a crisis of managing water so badly that billions of people - and the environment - suffer badly" (The World Water Vision Report).

In the field of Environmental Engineer treating wastewater for reuse has become an accepted and reliable technical solution to address water scarcity problems around the world and to lead to a significant saving of freshwater [1].

Main objective of wastewater reclamation and reuse projects is to produce water of different quality depending on its future use. Concerning wastewater reclamation for non-potable uses, which do not require drinking water quality standards, treated water can be employed in agricultural and landscape irrigation, industrial applications, environmental applications (surface water replenishment, and groundwater recharge), recreational activities, urban cleaning, construction, etc… [10].

In this direction, wastewater treatment plants (WWTPs) have been considered essentially while designed by incorporating new technologies and processes to treat water and achieve a sufficient water quality to minimize the environmental impact when discharging water into natural water system, allowing the natural self-purification processes [1].

In Figure 1.2, a possible WWTPs flow diagram is shown: the first three steps are typically displayed in all WWTP (pretreatment, primary and secondary treatment) while the last one can change from one plant to other. These stages consist in a mix of physical, chemical and biological treatments with the aim of remove suspended solids, organic matter, pathogenic bacteria and nutrients from wastewater [1].

In despite of the exertion the global community is putting to promote enhanced wastewater treatment and water reuse, nowadays only 0,5-2.4% of consumed water comes from wastewater recycling due to critical factors like the high economic cost of recycling, the insufficient legal frameworks on water quality requirements and the presence of organic micropollutant [2].

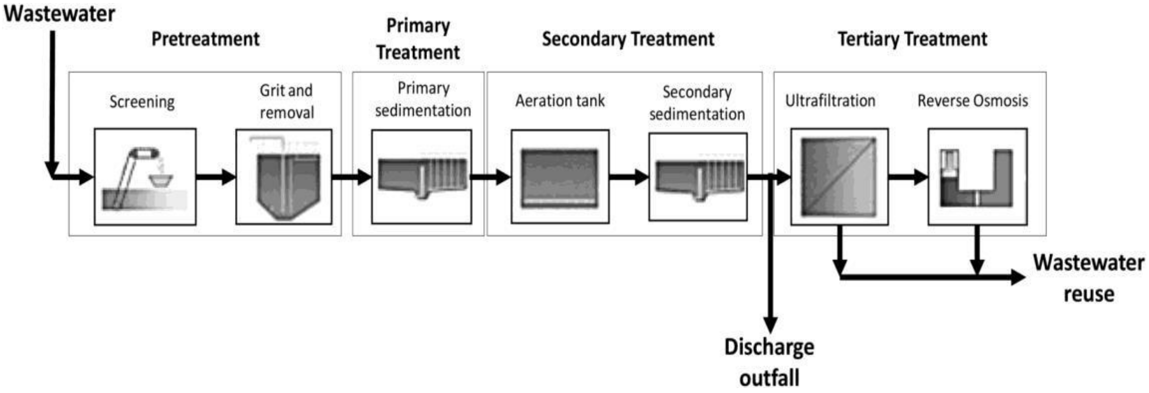


Figure 1.2. Possible WWTP process configuration [1].

1.3 Emerging contaminants

Over the last 20 years there has been a growing concert of the scientific community regarding the presence of new compounds in wastewater and aquatic environments called “emerging pollutants”, which have been defined by the Environmental Protection Agency of United States (US EPA) as “new products or chemicals without regulatory status and whose effects on environment and human health are poorly understood” [11].

These compounds, also called “micropollutants” due to the fact they are typically detected at trace levels (ng L^{-1} to µg L^{-1}), may be classified in the following six major groups (Table 1.I) [2].

Even though the MPs’ concentration in water bodies is low, an overall understanding of their behaviour and a proper regulation is necessary due to their resistance to conventional wastewater treatments and their potentially toxicity, bioaccumulation and environmental persistence [10].

Table 1.I. Summarize of MPs and their main sources in aquatic environment system [2].

Group	Subgroup	Main MP sources
Pharmaceuticals	Antibiotics Anticonvulsants Lipid regulator Non-steroidal anti-inflammatory drugs	Domestic WW (from excretion) Hospital effluence Run-off from Concentrated Animal Feeding Operations (CAFOs) and aquaculture
Personal care products	Fragrances Disinfectants Insect repellent	Domestic WW (from bathing, shaving, spraying, swimming etc...)
Steroid hormones	Oestrogens	Domestic WW (from excretion) Run-off from CAFOs and aquaculture
Surfactants	Non-ionic surfactants	Domestic WW (from bathing, dishwashing, laundry etc…) Industrial WW (from cleaning dumping)
Industrial chemicals	Plasticizers Flame retardants	Domestic WW (from materials leaching)
Pesticides	Insecticides Herbicides Fungicides	Agriculture runoff Domestic WW (from gardens and roadways dumping)

1.4 Advanced Oxidation processes

Advanced Oxidation Processes (AOPs) are treatment techniques that have been demonstrated to be a good option for the elimination of micropollutants from wastewaters, which are not completely removed with conventional processes in wastewater treatment plants [12]. This family of processes are based on the generation of powerful reactive species, mainly hydroxyl radical ($HO\cdot$), which are able to undergo oxidative reactions with most chemical species typically present in actual water matrices. Different techniques may be used for $HO\cdot$ generation, although all of then often employ a radical precursor alone or in combination with a catalyst, an energy source, or both. Under particular conditions these radical driven oxidation techniques can lead to partial oxidation or mineralization of organic compounds, generating this way inorganic ions as final products [10]. In practice, however, transformation products typically more biodegradable and less toxic are formed and released with the treated effluent.

1.4.1 Fenton and photo-Fenton processes

The Fenton process is one of the most well-known AOPs, having been extensively studied for the degradation of recalcitrant organic contaminants in numerous different water matrices [13]. It was discovered by Henry J.H. Fenton who found the high enhancement of $HO\cdot$ production employing iron salts (Fe(II)) as catalyst of hydrogen peroxide (H_2O_2) decomposition showing the best performance at a pH value of 2.8 [10], described by the following reaction (R1.1).

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO\cdot + OH^- \qquad \text{(R1.1)}$$

Photo-Fenton process consists in a modification of the conventional Fenton system by inclusion of UV-Vis light. The effect of this energy source is increasing the efficiency of the process by enhancing the $HO\cdot$ production, which is the result of promoting a faster iron reduction to the most reactive species (Fe(III) to Fe(II)) [1]. Under a certain irradiation wavelength (180 to 410 nm), an extra path to the HO· generation is thus permitted, which lead to faster oxidation reactions and, according to reaction 1.2, a continuous recycle of ferrous cation [14].

$$Fe(III) + H_2O + light \rightarrow Fe(II) + HO\cdot + H^+ \qquad \text{(R1.2)}$$

Regarding both AOPs', the processes showed up to be very convenient as an environmental application due to the cheapness and non-toxicity of H_2O_2 and iron salts combined to the potentially non-harmful residues produced by this reaction [1].

1.4.2 Potential modifications of conventional Fenton and photo-Fenton

One of the main operating costs in Fenton and photo-Fenton processes are the consumption of chemicals for adjusting the pH to 2.8 and its neutralization after treatment, which rise the interest among the scientific community to enhance process competitiveness considering low doses of iron and H_2O_2 at neutral pH [12,15]. However, at circumneutral pH the process exhibits poor performance. In particular, Fe(III) present in solution as $Fe(OH)_{3(s)}$ undergo precipitation [14], slowing the rate of hydroxyl radical's generation and decreasing the efficiency of this treatment [16]. This fact makes unattractive the application of this technique at full-scale. Concerning photo-Fenton particularly, it is necessary to consider that the application of artificial light increase the process cost due to the power consumption involved [1].

1.4.2.1. Fenton and Photo-Fenton treatment at neutral pH: use of chelating agents

A possible solution to the problems linked to treat effluents at circumneutral pH could be solved by adding compounds able to form stable complexes with iron [13]. Agents such as mono-, poly-, or amino-carboxylic acids such as Ethylenediamine-N, N-disuccinic acid (EDDS) or ethylenediaminetetraacetic acid (EDTA) have been considered due to their stability at neutral pH, photo-chemical effectiveness, biodegradability and ability to increase the absorbance capacity of iron aquo-complexes in the visible region when used as an organic ligand of iron [15]. Consequently, these effects could substantially improve photo-Fenton economics.

1.4.2.2. Radiation source: solar light

As mentioned before, the Fenton variation using the incorporation of light could be unattractive because of a potential lack of counterbalance between the photo-Fenton efficiency and the higher total cost due to power usage.

The viability of using natural solar light as a source of radiation has been investigated so far by the scientific community to promote a sustainable improvement of the process. Indeed, it has been considerate a very promising possibility which can be applied to photo-Fenton process to promote efficiency increase and cost reduction [14].

2. JUSTIFICATION OF THE PROJECT

Being WW reutilization considered by the scientific community to be an important source of irrigation in the scarcity water scenario, photo-Fenton is one of AOPs for water treatment solution, which effectiveness makes really interesting the possibility to extend its application avoiding the acidification of the influent and following neutralization. In this way, the strategy in which the thesis had been focus on shows the employment of some widely used organic fertilizers, iron chelates which may potentially be used in photo-Fenton treatment to avoid the iron precipitation at neutral pH.

Despite the fact that several studies in the literature report the use of iron chelates in photo-Fenton at neutral pH, the mechanisms by which the process works still remain unclear. There are evidences of the reactivity of iron chelates with sunlight radiation and dissolved oxygen, and how these processes could potentially lead to the generation of other reactive oxygen species (ROS) in addition to hydroxyl radical generated in the classical Fenton or photo-Fenton. These species could have significant environmental implications if they are also formed in aquatic ecosystems after use in crop irrigation.

This study is based on the investigation on the mainly involved reaction mechanisms in the solar photo-Fenton process at neutral pH. This includes data about ROS formation because of the interactions between all the involved agents, that is, iron chelates, hydrogen peroxide, sunlight and potentially dissolved oxygen.

To achieve this general goal, the following specific objectives are defined:

- Assessing three different commercially available chelating agents as EDTA (*Ethylenediaminetetraacetic acid)*, DTPA (Diethylenetriamine pentaacetate), EDDS (Ethylenediamine-N, N'-disuccinic acid) in the application of photo-Fenton treatment at both acid and circumneutral pH for the degradation of one model organic pollutant (SMX), with the aim of understanding each one’s catalytic activity.
- Studying the mechanisms taking place when iron chelates made with organic fertilizers interact with hydrogen peroxide, UV radiation coming from sunlight and dissolved oxygen. To do that, analysis of the influence of all these agents on the process performance were conducted, including several scavenging tests in ultrapure water solutions, in order to avoid the influence of other compounds typically found in wastewater, such as dissolved organic matter.
- Conducting an economic evaluation concerning the application of the photo-Fenton technique at neutral pH using sun radiation as source of light to comprehend the real possibility of introducing the process at industrial scale in a small WWTP.

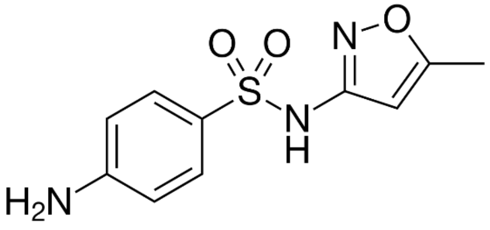
3. MATERIALS, ANALYTICAL METHODS AND PROCEDURES

3.1 Chemicals and reagents

The organic fertilizers involved in this study were three: DTPA-Fe (7% of iron), EDTA-Fe (13.3% of iron) both purchased from Phygenera, Germany, and EDDS-Na solution, purchased from Sigma-Aldrich.

Sulfamethoxazole (SMX) is the reference compound used to evaluate the performance of the oxidative treatments. It is a sulphonamide antibiotic which is effective against both, gram negative and positive bacteria purchased from Sigma-Aldrich (Spain). Its main chemical data have been showed in the Table 3.I.

Table 3.I. Main chemical data of Sulfamethoxazole compound.

Chemical formula	$C_{10}H_{11}N_3O_3S$
Chemical name	4-Amino-N-(5-methyl-3-3isoxazolyl) benzenesulfonamide, N^1-(5-Methylisoxazol-3-yl) sulphanilamide
Chemical structure	
Molar mass	253.28 g mol^{-1}
CAS number	723-46-6

The catalase from bovine liver employed to stop the reaction and tert-Butanol (99,7%) used as a radical hydroxyl scavenger were also bought from Sigma-Aldrich.

Hydrogen peroxide solution used as oxidant (30% w/v), sodium hydrogen carbonate, acetonitrile, orthophosphoric acid and ferrous sulphate were acquired from Panreac Quimica. The filters used for sample preparation were Chmlab Group 0.45 µm (pore size) PVDF membrane filters and Minisart-RC 0.20 µm (pore size) nylon membrane filters.

A summary about all the chemical reagents has been displayed in Table 3.II.

Table 3.II. Summary of all chemical reagents used in the investigation.

Name	CAS No.	Formula	Company	Purity (%)	Used in/for
Acetonitrile	75-05-8	CH_3CN	Fischer Chemical	99.80	HPLC analysis
Acetic acid glacial	64-19-7	CH_3COOH	Panreac Quimica	99,7	Buffer in iron determination
Ammonium acetate	631-61-8	CH_3COONH_4	Panreac Quimica	96,0	Buffer in iron determination
Ammonium metavanadate	7803-55-6	H_4NO_3V	Sigma Aldrich	99	H_2O_2 determination
Ascorbic acid	50-81-7	$C_6H_8O_6$	Panreac Química	91	Totally Fe determination
DTPA	67-43-6	$C_{18}H_{23}N_3O_{10}$	Sigma Aldrich	99	Iron chelate
DTPA-Fe (7%)	19529-38-5	$C_{14}H_{18}N_3O_{10}FeNa_2$	Phygenera	100	Iron chelate
EDDS-Na3	57653-48-5	$C_{10}H_{13}N_2Na_3O_8$	Sigma Aldrich	35 w/w	Iron chelate

EDTA-Fe (13,3%)	18154-32-0	$C_{10}H_{12}N_2O_8FeNa \times 3H_2O$	Phygenera	100	Iron chelate
Hydrogen peroxide	7722-84-1	H_2O_2	Merck	30 w/w	Photo-Fenton
Iron (II) sulphate heptahydrate	7782-63-0	$H_{14}FeO_{11}S$	Panreac Química	30	Photo-Fenton
Liver bovine catalase	9001-05-2	$C_9H_{10}O_3$	Sigma Aldrich	-	To avoid further reactions
Nitrogen	7727-37-9	N_2	Abelló Linde (Spain)	99,99	To remove O_2
Orthophosphoric acid	7664-38-2	H_3PO_4	Panreac Química	85	HPLC analysis
Sodium Hydrogen Carbonate	144-55-8	$NaHCO_3$	Panreac Química	99	pH maintenance
Sodium Hydroxide	1310-73-2	$NaOH$	Panreac Química	98	pH adjustment
Sulfamethoxazole	723-46-6	$C_{10}H_{11}N_3O_3S$	Sigma Aldrich	100	Model compound
Sulfuric acid	7664-93-998	H_2SO_4	Panreac Química	98	pH adjustment
Ter butanol	75-65-0	$C_4H_{10}O$	Sigma Aldrich	99,7	Hydroxyl radical scavenger
1,10-phenanthroline	66-71-7	$C_{12}H_8N_2$	Sigma Aldrich	99	Fe(II) determination

3.2 Laboratory experiments

The dissolution was prepared according to the percentage of iron content of each commercial organic fertilizers with ultra-pure water. Therefore, to have 5 mg L^{-1} of iron in solution, the quantities of iron chelated involved were 0.072 g L^{-1} DTPA-Fe and 0.067 g L^{-1} EDTA. Concerning EDDS-Na solution, a molar ratio of 1:1 (EDDS:Fe (II)) was selected based on literature [19]. To ensure a good chelation in the case of EDDS experiments, this compound was dissolved first and then iron was added.

When H_2O_2 was involved, a 5:50 mass ratio of Fe:H_2O_2 was followed to optimize the Photo-Fenton process. In this way, 0.17 mL of concentrated H_2O_2 solution were employed and added just before the reaction began. A concentration of 1 mg L^{-1} of SMX was selected to conduct the study under realistic conditions. Finally, sodium bicarbonate was added as a buffer to ensure pH stability during the process. The duration of the experiments was 120 min, with samples being taken out from the tank after 0.5, 3, 5, 10, 15, 20, 30, 45, 60, 90, 120 minutes, respectively. Catalase was employed in each sample to stop the reaction (10 µL of catalase (200 mg L^{-1}) in 5 mL of each sample). 0.20 µm filters were employed to ensure a proper analysis of chelated iron whenever the total iron content needed to be analysed. In these measurements, ascorbic acid was added to the sample to make possible the total chelated iron measurement through Fe(III) to Fe(II) reduction.

3.3 Main techniques and analytical instruments

3.3.1 Determination of SMX concentration

The concentration of SMX in solution was quantified by High Performance Liquid Chromatography (HPLC Infinity Series, Agilent Technologies) (Figure 3.1). The analysis has been carried out according to the absorbance of SMX, the wavelength of the UV detector was set at 270 nm, the flow rate was kept at 1 mL min^{-1} and the injection volume was set to 100 µL.

The HPLC column used was a Teknokroma C-18 Mediterranea Sea (250 mm x 4.6 mm; 5μm particle size) and the mobile phase consisted of a 60:40 solution of acetonitrile and acidified water, respectively.

Figure 3.1. HPLC UV Infinity Series (Agilent Technologies) used for measuring the SMX residual concentration in solution.

3.3.2. Hydrogen peroxide consumption determination

The monitoring of H_2O_2 was performed through colorimetric method of metavanadate [19], a spectrophotometric procedure used to measure the H_2O_2 residual concentration during photodegradation reactions. It is based on the reaction of H_2O_2 with ammonium metavanadate (5.144 g L^{-1}) in acidic medium (19.2 mL H_2SO_4 L^{-1}), which lead to an orange coloration due to the VO_2^{3+} generation species. The procedure consists of adding 1.5 mL of sample to a 1.5 mL of an ammonium metavanadate solution and measure the

VO_2^{3+} generated species at maximum absorbance at 450 nm with a Hach Lange DR6000 UV-Vis spectrophotometer (Figure 3.2).

Figure 3.2. Spectrophotometer UV-Vis Hach Lange DR6000 employed in absorbance measurements.

3.3.3. Dissolved iron measurement

The total iron concentration in solution was determined according to the standard 1,10-phenantroline spectrophotometric procedure (ISO 6332). 4 mL of sample were mixed with 1 mL of 1 g L^{-1} 1.10-phenantroline and 1 mL of acetic acid buffer (pH=4) plus ascorbic acid was added in order to reduce ferric iron Fe (III) to ferrous iron Fe (II). The intensity of the red colour that Fe (II) cations form with 1.10-phenantroline gives information about the iron precipitated in solution. The absorption of this complex measured at 510nm by spectrophotometer Hach Lange DR6000 UV-Vis (Figure 3.2) is proportional to ferrous iron concentration.

3.4 Experimental device: Solar light simulator

Solar light was simulated with a solar spectrum simulation chamber (Xenoterm-1500RF, CCI) composed by a Xenon lamp of 1.5 kW (Philips XOP 15-OF 1CT) which irradiates light within a wavelength range of 290-400 nm to a DURAN glass tubular photoreactor (25 cm length x 2 cm diameter).

A scheme of the solar simulator system is shown in Figure 3.3. In a typical experiment, the 1L solution contained into the reservoir thermostatic magnetically stirred tank was continuously pumped by a peristaltic pump (Ecoline VC-280II, Ismatec) into the solar simulation chamber, and then recirculated back. The temperature was controlled by Haake C-40 bath and keep constant at 25ºC.

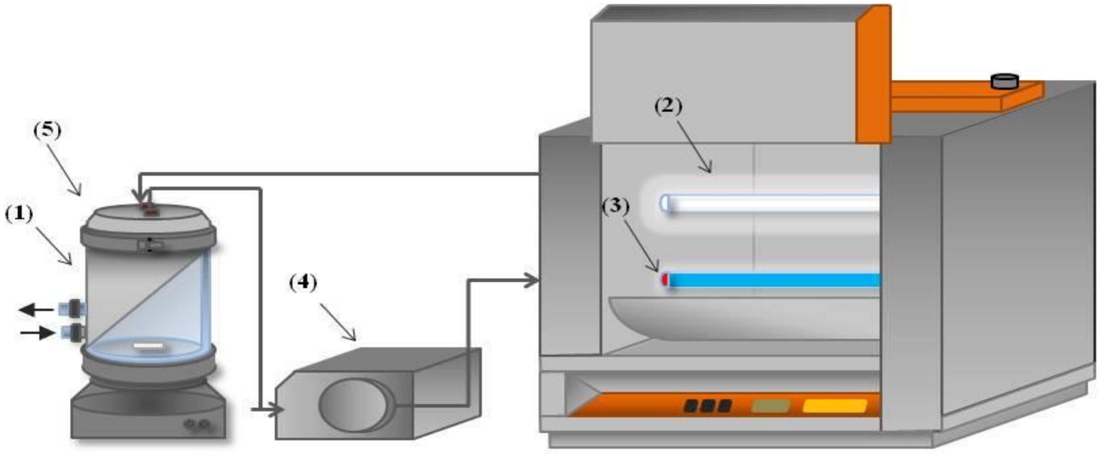


Figure 3.3. Solar spectrum simulation system Xenoterm-1500RF, CCI: (1) reservoir thermostatic tank, (2) Xenon lamp, (3) tubular reactor, (4) peristaltic bomb, (5) samples access [9]

The photon flow was determined by o-Nitrobenzaldehyde actinometry [19] and resulted to be $6.60 \cdot 10^{-7}$ Einstein $L^{-1}s^{-1}$, considering the molar absorption of o-Nitrobenzaldehyde at medium wavelength of 367 nm (ε: 128 L mol^{-1} cm^{-1}), the quantum yield (ϕ) of 0.5, the volume solution of 1L and the cylinder area of 0.0154 m^2.

4. RESULTS AND DISCUSSION

As mentioned in paragraph 3.2, sodium bicarbonate has been employed as a buffer to maintain the pH stable in all the tests. Bicarbonate scavenger effect over hydroxyl radical (assuming that most of the model pollutant abatement proceeds via OH• oxidation) has been imposed to be less than 5%. In relation to this consideration, the employed concentration of bicarbonate in all experiments was 100 mg L^{-1} of $NaHCO_3$, which according to Eq 4.1 represents a scavenging effect of 2.9%.

$$\%\,Scavenger\ Effect = 100 * \qquad \text{(Eq 4.1)}$$

$$* \frac{k_{OH,HCO_3^-} * \ [HCO_3^-]}{(k_{OH,HCO_3^-} * \ [HCO_3^-]) + (k_{OH,DTPA-Fe)} * [DTPA - Fe]) + (k_{OH,SMX} * [SMX]) + (k_{OH,H_2O_2} * [H_2O_2])}$$

4.1 Comparison of Fe (III) complexes on photo-Fenton process

Due to the fact that EDDS-Fe and EDTA-Fe complexes have been deeply studied from scientific community during the last years, a different organic fertilizer (DTPA-Fe) has been tested and compared to the others in order to assure it could be used as iron chelates whereas would be involved in agriculture water reuse.

A first investigation over the three organic fertilizers selected was done in the SMX degradation under photo-Fenton condition and neutral pH. Then, Fenton and photo-Fenton's reaction at neutral pH have been compared while an organic compound like DTPA-Fe has been introduced in the system. The mechanisms of reactions are very similar to those in the conventional system (R1.1 and R1.2, respectively). Photo-Fenton process can be described by all three following reactions (R 4.1, R 4.2, R 4.3), and since Fenton is already included in photo-Fenton, R5 and R6 are the reaction which will explain it:

$[DTPA\text{-}Fe(III)]^- + h\nu + H_2O \rightarrow [DTPA\text{-}Fe(II)]^{2-} + H^+ + OH\cdot$ (R 4.1)

$[DTPA\text{-}Fe(II)]^{2-} + H_2O_2 \rightarrow [DTPA\text{-}Fe(III)]^- + OH\cdot + OH^-$ (R 4.2)

$[DTPA\text{- }Fe(III)]^{-} + H_2O_2 \rightarrow [DTPA\text{- }Fe(II)]^{2-} + 2H^{+} + O2^{\cdot -}$ (R 4.3)

According to R1.2, hydroxyl radical production in this system appears to be proportional to the iron availability, and since EDDS is less strong chelate this favors the iron to be ready to react with H_2O_2.

In Table 4.I the main information of the three chelates complexes employed in the experiments are shown in terms of formula, chemical structure and molecular weight. Chemical structure gives information about the stability of the complex in relation to strength, functional groups, pH and number of chelates interactions.

DTPA-Fe and EDTA-Fe complexes present a robust structure, pentagonal bipyramidal and octahedral geometry, respectively. Regarding EDDS-Fe complex, it is less stable than the other two, probably making the iron to be less protect by the chelator while more available in solution to react with H_2O_2.

The experiments were carried out in an ultrapure water matrix. Based on literature, the optimum mass ratio Fe: H_2O_2:SMX used for the tests were 5:50:1 [20].

From the results showed in Figure 4.1, the total removal of SMX during the 120 min experiment was only achieved when employing the EDTA-Fe complex, while EDDS-Fe and DTPA-Fe reached the 94.7% and 90.1%, respectively.

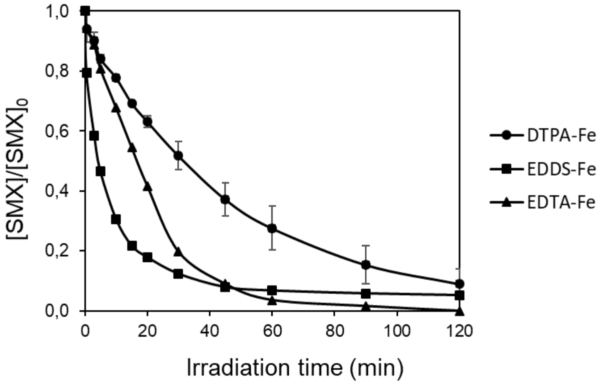
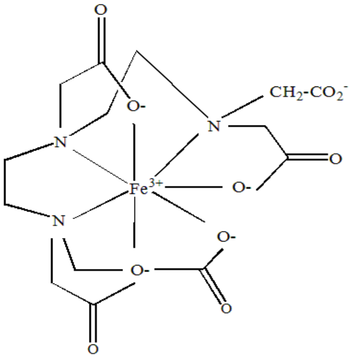
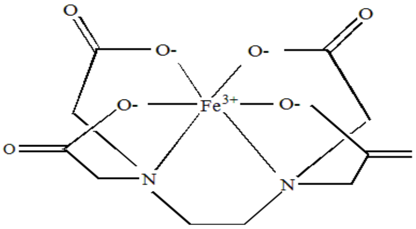
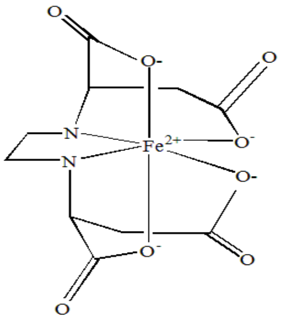


Figure 4.1 Comparison of SMX removal catalyzed by three Fe (III) chelate agents by means of photo-Fenton process at neutral pH, T=25ºC, SMX= 1 mg L^{-1}, *H_2O_2= 50* mg L^{-1}.

Table 4.I. Main characteristic of iron complexes applied to photo-Fenton process at neutral pH

Compound	**Molecular formula**	**Chemical structure**	**Molecular weight (g mol^{-1})**
DTPA-Fe	$C_{14}H_{18}N_3O_{10}FeNa_2$		490.20
EDTA-Fe	$C_{10}H_{12}N_2O_8FeNa\cdot 3H_2O$		421.10
EDDS-Fe	$C_{10}H_9N_2FeNa_3O_8$		409.85

As can be shown in Table 4.II, first-order kinetic constants of SMX abatement were calculated for experiments conducted with the three organic fertilizers in a time range between 0-15 min, according to Eq 4.2.

$$-ln\frac{(Cf)}{(Co)} = k\ t \qquad \text{(Eq 4.2)}$$

The kinetic rate has been influenced by iron precipitation and stability constant of the complexes, closely linked to the chemical structure of the chelate agents. It has been demonstrated that a higher stability constant of iron complex is proportional to a strongest chemical structure and a lower reaction rate of MP (Table 4.II).

In fact, complexes' stability constant (k_{stab}), which is different for every chelate, gives information about the stability of the complex in solution so iron availability for reacting with H_2O_2 in photo-Fenton process. Indeed, when iron precipitates in solution as ferric hydroxide form ($Fe(OH)_3$) would be no longer possibility to be involved in reaction.

As EDDS-Fe(II) stability constant was not found, it has been supposed following other's chelates trend to be much lower than EDDS-Fe(III). Such a tendency explained the relation between the high precipitation rate of iron in solution and its fast kinetic, hence the decreasing on the process efficiency thus the impossibility of the complex for reaching the total removal of SMX compound [22].

DTPA-Fe complex has been chosen as chelate complex model in this investigation due to its stability in solution and kinetic, which is not very fast like the others, permitting to better study the mechanism of the photo-Fenton process at neutral pH.

Table 4.II. Different parameters attained over pure water for photo-Fenton process for three different chelate agents calculated for the first 15 minutes of experiment.

Chelating agents	**k** **(min^{-1})**	**R^2**	**Precipitated iron** **(%)**	**k_{stab}** **(Ligand-Fe(II))**	**k_{stab}** **(Ligand-Fe(III))**
DTPA-Fe	0.017	0.9974	0	16.55	28.60
EDTA-Fe	0.039	0.9950	0	14.33	25.10
EDDS-Fe	0.096	0.9641	17.5	-	22.0

4.2 Effect of iron chelation, H_2O_2 and sunlight presence in SMX degradation

Four different blank tests were done at neutral pH by means of UV-Vis irradiation in order to estimate the SMX removal and compare it while testing in distinct conditions (Table 4.III). Mass ratio 1:50 of SMX:H_2O_2 was followed while H_2O_2 was used for reaction.

Table 4.III. SMX abatement in four different tests at neutral pH condition, under UV-is irradiation, T=25°C, SMX=1 mg L^{-1}, *H_2O_2= 50* mg L^{-1}.

Experiment	**Radiation (*hv*)**	**H_2O_2**	**DTPA**	**SMX removal (%)**
1	√			0
2	√	√		9.7
3	√		√	0
4	√	√	√	11.5

Firstly, photolysis experiment was conducted to study the light effect alone, leading to a 0% degradation of the model compound. Meanwhile, the addition of H_2O_2 combined with light raised the SMX removal to 9.7%, apparently implying ROS generation and their slight involvement to degradation. Such a trend can be explained from Reaction 4.4 valid for H_2O_2 absorbance range of 254-299 nm [24]:

$H_2O_2 + hv \rightarrow OH\cdot$ (R 4.4)

Secondly, the introduction of non-chelated DTPA has been investigated to better understand the compound removal reaction while organic ligand is not bonded to iron. The experiment revealed that DTPA alone did not enhance the SMX removal, which means that it did not led to additional pathways of oxidant species generation. Indeed, almost same percentages of SMX degradation were shown while no chelated DTPA was introduced in solution: 0% and 11.5% without and with the H_2O_2 presence, respectively.

Following this line, in Figure 4.2, a comparison between the total absorption spectrums of the two DTPA species (Fe chelated and not) have been reported to demonstrate, when light is employed, that chelation ensured an excitation of the iron complex showing the maximum at 258nm.

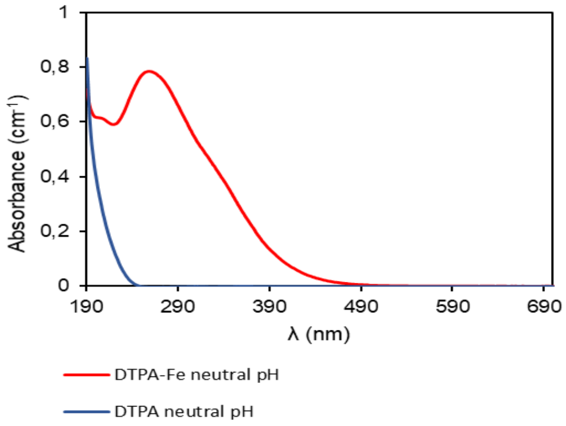


Figure 4.2. Absorption spectrum comparison between DTPA-Fe complex and no chelated DTPA.

The positive effect of the DTPA-Fe(III) complex on photo-Fenton process was checked and compared, in terms of SMX degradation efficiency, with DTPA (without Fe chelated) at neutral pH.

The results are reported in Figure 4.3 and demonstrate that compound degradation can be possible only when the iron chelate is present, since iron remains available in the solution and can react with hydrogen peroxide showing the way to a possible path of ROS species generation thus leading to a higher efficiency of the process. In this way, when both DTPA-Fe(III) chelate and H_2O_2 were employed, SMX degradation hugely raised from 11.5% to 90.1%.

At the same time, the 11.5% SMX degradation reached without iron complexes presence is confirmed to be achieved by the ROS species yielded as a consequence of H_2O_2 and light interaction.

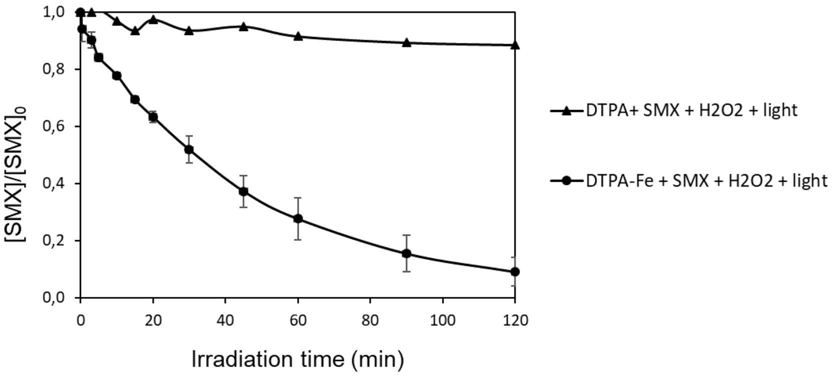


Figure 4.3. Effect of DTPA iron complex on the degradation of 1 mg L^{-1} *of SMX compared with no chelated DTPA at neutral pH conditions, UV-is irradiation, T= 25°C, H_2O_2= 50* mg L^{-1}.

4.3 Oxygen effect

An investigation over the oxygen effect has been done in order to understand the impact of its presence on the process performance. Tests were carried out with and without N_2 bubbling, which in the second case was conducted for 30 min before and during the whole experiments.

According to the results reported in Figure 4.4, the SMX degradation decreased under anoxic conditions. In fact, in the case of nitrogen saturated solution, SMX removal dropped from 90.1% to 69.2% while hydrogen peroxide was also employed, and from 30.1% to 10.2% while only UV-is radiation was applied.

Such a trend indicates that oxygen can enhance the degradation of SMX as it is involved in the reaction's mechanism. Following this line, two hypotheses were considered to explain the obtained 30.1% SMX removal.

Firstly, the degradation is totally achieved through R 4.1, which led to $OH\cdot$ generation even in absence of both O_2 and H_2O_2.

Secondly, the observed SMX removal might be justified by the generation of radical iron complex species due to evolvement of light as can be show by reactions R 4.5 and R 4.6:

$[DTPA\text{- }Fe(III)]^{-} + hv \rightarrow [DTPA\text{- }Fe(II)]^{*2-}$ (R 4.5)

$[DTPA\text{- }Fe(II)]^{*2-} \rightarrow Fe\ (II) + DTPA^{\cdot 3-}$ (R 4.6)

Hence, from R 4.5 in aerobic condition, $[DTPA\text{-}Fe(II)]^{*2-}$ could lead to the generation of hydroxyl radical, previous superoxide radical species formation ($O_2^{\cdot -}$) (R 4.7), even if the kinetic of reaction is very slow (0,095 $M^{-1}\ s^{-1}$) [25].

$[DTPA\text{- }Fe(II)]^{*2-} + O_2 \rightarrow [DTPA\text{- }Fe(II)]^{3-} + O_2^{\cdot -}$ (R 4.7)

Superoxide radicals allow a very fast transfer from iron(III) to iron(II) (R 4.8) and a possible generation of hydrogen peroxide (R 4.9), which let the maximum removal of SMX compound (90.1%) by R5, justified by a bigger $OH\cdot$ production.

$[DTPA\text{-}Fe(II)]^{3-} + O_2^{\cdot -} \rightarrow [DTPA\text{-}Fe(II)]^{2-} + O_2$ (R 4.8)

$O_2^{\cdot -} + O_2^{\cdot -} + H_2O \rightarrow H_2O_2 + O_2 + 2OH^{-}$ (R 4.9)

To what concern the possible situation in anoxic condition, from R 4.6, $DTPA^{\cdot 3-}$ could be the main contributor to the total SMX degradation observed in this experiment, also taking into account that, at neutral pH tests, Fe(II) decreased and precipitated in the form of ferric hydroxide form ($Fe(OH)_3$) (Figure 4.4).

Nevertheless, $DTPA^{\cdot 3-}$ presence is only involved at minimum in compound degradation, explained by the 10.2% of SMX removal while H_2O_2 and O_2 were not employed. In addition, the almost 20% SMX degradation difference showed up while comparing aerobic and anoxic experiments (5 and 6 in Table 4.IV, respectively) is due from the main photo-Fenton reaction.

A supplementary test consisted in hydroxyl radical scavenger (tert butanol, tBOH) application was conducted to better understand if the total degradation of compound can be assumed to proceed completely via hydroxyl radical oxidation. In this case, the SMX removal was 0% (Figure 4.4), so confirming that the total SMX disposal is caused by OH·.

Finally, $DTPA^{\cdot 3-}$ species did not attack directly the compound, but it led, in light presence, to hydroxyl radical generation (R 4.10) which is the oxidant species mainly responsible of SMX disposal.

$DTPA^{\cdot 3-} + OH^{-} \rightarrow DTPA^{4-} + OH\cdot$ (R 4.10)

However, it is important to say that the degradation of SMX by OH· from R9 would be minimum as iron precipitation during tests was very low (Table 4.IV), making least possible the generation of $DTPA^{\cdot 3-}$ species.

As mentioned in 4.1, the high iron precipitation is proportional to high compound degradation due to the elevated amount of OH· formed and its no selectivity nature in attacking every compound present in water matrix.

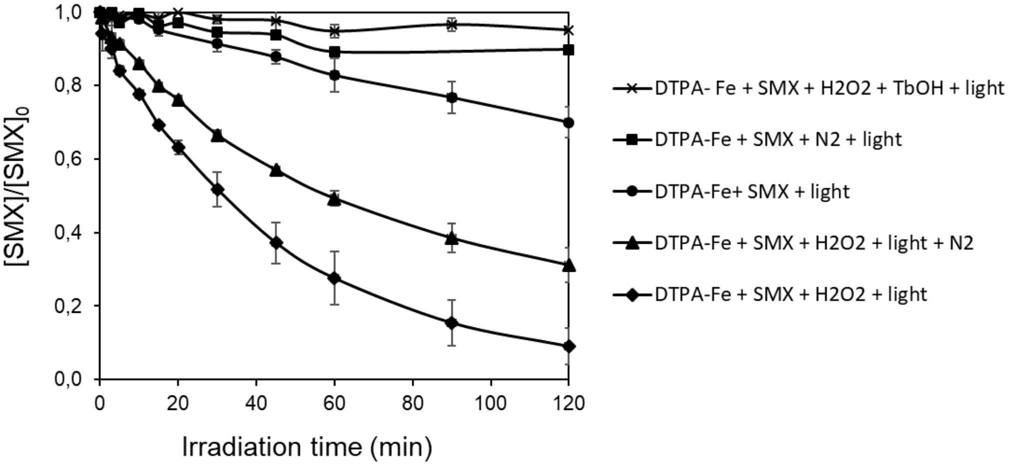


Fig 4.4. Comparison of DTPA iron complex on the degradation of 1 mg L^{-1} *of SMX in anaerobic, aerobic and tBOH presence condition, tested at neutral pH, UV-is radiation presence, T=25 °C,* H_2O_2*= 50* mg L^{-1}*.*

Table 4. IV. Correlation between precipitated iron and SMX removal in photo-Fenton test at neutral pH.

N°	Experiments	Precipitated iron (%)	SMX degradation (%)
5	DTPA-Fe + SMX + light	4.92	30.1
6	DTPA-Fe + SMX + N_2 + light	3.56	10.2
7	DTPA-Fe + SMX + H_2O_2 + light	10.15	90.1
8	DTPA-Fe + SMX + H_2O_2 + N_2 + light	10.31	69.2
9	DTPA-Fe + SMX + H_2O_2 + N_2 + tBOH + light	0	0

4.4 Effect of solar light

In order to investigate the effect of the solar light and to promote the enhancement of the process at neutral pH, dark-Fenton and photo-Fenton processes were compared at same concentration condition: 1 mg L^{-1} of SMX, 50 mg L^{-1} of H_2O_2 and 5 mg L^{-1} of Fe.

As mentioned in 1.4.1, the energy source introduction in photo-Fenton process allowed an enhancement on the efficiency of the process by improving the HO· production. Also, from R 1.1, solar light promoted a faster iron reduction to the most reactive species (Fe(III) to Fe(II)), which would justify the higher degradation of SMX compound in photo-Fenton experiments and, at the same time, a higher precipitation of iron spotted [1] (Table 4.V).

Table 4.V. Correlation between precipitated iron and SMX removal in photo-Fenton test at neutral pH.

Reaction	**Chelating agents**	**Precipitated iron (%)**	**SMX degradation (%)**
Fenton	DTPA-Fe + SMX + H_2O_2	5.18	67.6
Photo-Fenton	DTPA-Fe + SMX + H_2O_2 + light	10.15	90.1

Following this line, the resulted reported in Figure 4.5 confirmed that photo-Fenton reaction is more efficient than dark-Fenton's one, as the SMX removal has counted to be 90.1% in front of 67.6%. Such a development would like to demonstrate that the production rate of hydroxyl radicals by the decomposition of H_2O_2 (R 4.4) when reacting with ferrous ions is improved by using solar light.

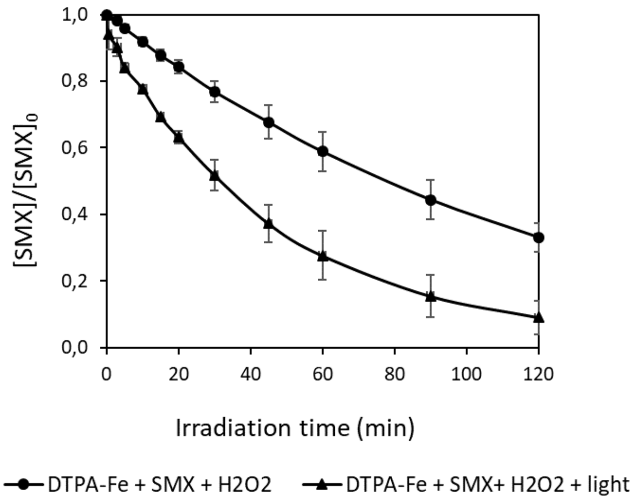


Figure. 4.5 Comparison between photo-Fenton and dark-Fenton processes at neutral pH condition in terms of SMX degradation by DTPA chelate.

5. ECONOMIC ANALYSIS

An economic assessment over the application of photo-Fenton at neutral pH was developed considering the possible ubication of a Raceway Pond Reactor (RPR) in WWTP in south of Spain to take advantage of the 12 hours of sun radiation availability per day. Furthermore, it has been considered that the tertiary treatment could be applied to a low-flow treatment line in WWTP or a small WWTP, which will be able to serve fertilized added water, ready to be use for agricultural purpose to the closest crop fields.

The solar radiation calculated to achieve the 80% of SMX compound removal was 3.28 kJ L^{-1}, considering a continuous WWTP capacity flow of 1200 m^3 day^{-1}. Presuming a constant solar radiation of 30 J m^{-2} s^{-1} [23], the RPR has been designed with 5 cm of liquid depth and an area of 3037 m^2. The hydraulic retention time (HRT) has been estimated taking into consideration the solar radiation needed for SMX abatement and RPR design parameters, counting to be 1.52 hours.

Concerning the total operation cost (OC), expressed in both annual and unitary cost can be summarized in Table 5.I. and has been evaluated from bibliography with equation 5.1 [23]:

$$OC = 0.2\ AC + Ce + Cr \qquad \text{(Eq 5.1)}$$

Where AC is the amortization, which also considered 20% of maintenance cost, Ce and Cr are the energy and the reagent's cost, respectively.

Operation cost has mostly been affected by the reactant cost, showing up to represent the 99,9% of the total investment (Table 5.I): DTPA Iron chelate (7%) appeared to be the most expensive one.

Energy cost has been computed reflecting to be unimportant (0.1% of total costs) (Table 5.I). As a matter of facts, it has only been influenced by wastewater pumping in reactor. Four dosing pumps of 50W and a centrifugal pump of 18W were took into consideration for the calculous, while electricity price has been counted to be 0,1 $kW^{-1}\ h^{-1}$ and the unitary power requirement 4 $W\ m^{-3}$ [23].

Moreover, the amortization cost has been calculated with the equation 5.2 [23] and showed up to be not significant:

$$AC = \frac{I}{L} \qquad \text{(Eq 5.2)}$$

Where the investment cost I depended on the cost per unit area (10 € m^{-2}) and the plant's life cycle of 20 years (L).

The economic estimation has determined the unitary total operation cost of 0,6 € m^{-3}, which would be even more affordable if the photo-Fenton treatment at neutral pH for reused water would be applied to a larger scale, leading to a reduction of DTPA iron complex price involved in the process at industrial scale.

Table 5.I Summary of total costs for a medium flow allied photo-Fenton treatment in WWTP.

RPR Total Cost	**Annual cost (€ year^{-1})**	**Unitary cost (€ m^{-3})**	**Percentage of the total cost (%)**
Amortization	1518.52	0,0035	0.01
Chemicals	288948.60	0.66	99,99
Energy	266.48	0.00061	0.09
TOTAL	289245.45	0.664	100

6. CONCLUSION

This paragraph consists on the main conclusions about this research aimed to evaluate the effect of Fe (II) and Fe (III) complexes in the photo-Fenton process at neutral pH in terms of SMX degradation due to ROS formation.

The principal points, based on the laboratory experimentation done, have been summarized to conclude that:

- Photo-Fenton application on the three iron complexes investigated (DTPA-Fe, EDDS-Fe, EDTA-Fe) have significant positive effect on the degradation of SMX compound, as its efficiency is higher if compared with other individual processes such as photolysis and dark-Fenton. This is justified by chelated agents' presence, which can stabilize Fe (III) in aqueous solution at neutral pH so preventing iron precipitation and make it available to react with H_2O_2. Being an organic fertilizer not completely studied by scientific community, DTPA-Fe complex has been identified as chelate model in this thesis. Its kinetic and molecular composition stability permitted to better observe the photo-Fenton reaction’s mechanism at neutral pH.

- Introducing tBOH in tests as HO· scavenger, it can be assured that the degradation of SMX compound have been always reached by means of HO·, oxidant powerfullest reactive species.
- The investigation over the oxygen effect showed it is significant contributor in the oxidation of SMX while permitting other ROS’ generation which are finally leading to hydroxyl radical formation.
- The H_2O_2 engagement in experimentation showed there could be more ways of removal of the SMX compound: from the straight generation of hydroxyl radical in reaction or the chance of either ROS ($O_2^{\cdot -}$) or intermediate species formation ($[DTPA\text{-}Fe(II)]^{*2-}$, $DTPA^{\cdot 3-}$), which would cease to hydroxyl radical yielding.
- The integration of light in process permits a continuous cycle of iron from the less reactive species (Fe(III) to the most reactive one (Fe(II)), which guaranteed an enhancement of the efficiency of photo-Fenton technique.
- Lastly, the economical estimation of wastewater treatment for water reuse by employing the solar photo-Fenton process at neutral pH demonstrated the possible inversion in WWTP and a plausible decrease of cost if applied at industrial scale since reactant’s values consist of 99% of total price.

Despite of the new COVID-19 situation brought us to investigation slackening by closing our UB laboratory and a considerable interruption of the investigation, I feel very proud of the hard work done and the results we achieved. The return to investigation was possible for the cohesion of the AOPs Team, its skills to work together has given me the opportunity to conclude all the experiments and the final project in 3 weeks.

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