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**“MICROPOLLUTANTS REMOVAL FROM NATURAL WATER APPLYING THREE
ADVANCED OXIDATION PROCESSES IN COMBINATION WITH NANOFILTRATION”**

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ABSTRACT

Introduction

During the last 30 or so years, the analytical and environmental chemistry has focused more or less exclusively on the “conventional contaminants” (CC), mainly pesticides, industrial chemicals, heavy metals etc. Although these contaminants pose a great threat to the environment when released, they only represent a small percentage of chemicals which can be detected nowadays in the environment. In the last decade due to the increasing sensitivity of analytical instrumentals, like gas chromatography coupled with mass spectrometry (GC-MS and GC-MS/MS) and liquid chromatography coupled with mass spectrometry (LC-MS, LC-TOF/MS, LC-MS/MS), which push the limit of quantification/detection further into the low nano-gram range, an ever increasing number of new organic substances have been found in waste water, natural water (surface water, drinking water and tap water) and even ground water. These new organic substances are considered to be potentially hazardous substances and their type and range of concentration in the environment may vary considerably and, apart from the priority contaminants, whose environmental risks are well documented, for the majority of these organic compounds does not exist any environmental quality data. In particular, special attention has recently been given to what are called emerging contaminants (ECs) which in the most of cases are microcontaminants, that is contaminants that are present in extremely low concentrations and have physical/chemical properties that make them extremely difficult to be removed by conventional treatment methods. The ECs are defined as a group of organic substances which are not subject to restrictions of any kind, but may be candidates for future regulations, depending on the investigative results on the effects on human health, aquatic life forms and their presence in the environment. A wide range of compounds are considered to be relevant emerging compounds such as: detergents, pharmaceutical products and its metabolites, personal care products, flame retardants, antiseptics, fragrances, industrial additives, steroids and hormones. These contaminants are present in waters in increasing concentrations up to $\mu\text{g L}^{-1}$ and can have huge impacts onto aquatic life and as a consequence onto human health in the long run. It may have even more impact onto humans, if waters, which contain these contaminants, are used for irrigation, as water scarcity becomes an ever increasing problem (note that if waters are subject to reuse they also must be disinfected). Possible ecological problems are microbiological resistance, accumulation in soils, bioaccumulation in plants and animals, feminization of higher organisms, as many of these substances have endocrine disrupting abilities. Unfortunately, the

principal characteristic of these contaminants is that they are hardly biodegradable and resist treatment by conventional sewage treatment plants and, even if these substances are biodegradable, their constant release into environment battles the degradation process. It is therefore important to degrade these contaminants prior to their release into the environment, and even more so if the water is reused for irrigation. So, alternatives to the conventional activated sludge treatment need to be employed. Among these, chemical oxidative treatments, and especially, Advanced Oxidation Processes (AOPs), are well known for their capacity for oxidizing and mineralizing almost any organic contaminant. These methods rely on the formation of highly reactive chemical species, $\cdot\text{OH}$ radicals (hydroxyl radicals), which degrade even the most recalcitrant molecules into biodegradable compounds. They are also characterized by their not-selective attack, which is a useful attribute for wastewater treatment and solution of pollution problems. The versatility of the AOPs is also enhanced by the fact that there are different ways of producing hydroxyl radicals, facilitating compliance with the specific treatment requirements. Nevertheless, technical applications are still scarce. As the process costs may be considered the main obstacle to their commercial application, several promising cost-cutting approaches have been proposed, such as integration of AOPs as part of a treatment train. In the typical basic process design approach an AOP pretreats non-biodegradable or toxic wastewater, and once biodegradability has been achieved, the effluent is transferred to a cheaper biological treatment. The key is to minimize residence time and reagent consumption in the more expensive AOP stage by applying an optimized coupling strategy. Other proposed cost-cutting measures are the use of renewable energy sources, i.e., sunlight as the irradiation source for running the AOP.

Fenton, Fenton-like and photo-Fenton are probably among the AOPs most widely applied to wastewater treatment and significant efforts have been invested in exploring the possibility of running them using solar irradiation.

Aims of the study

This work has the purpose to specifically study the efficiency of three advanced oxidation processes, such as solar mild photo-Fenton (pH 5-6, $5 \text{ mg L}^{-1} \text{ Fe}^{2+}$, $25 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$), solar mild photo-Fenton with EDDS (S,S')-Ethylenediamine-(N,N')-disuccine acid trisodium salt solution (35% w/v) (which allows for operation at $\text{pH} > \text{optimum pH}$ for photo-Fenton process (2.8-3.0), since it forms complex with the iron making it available for the photo-

Fenton process, avoiding iron precipitation, which occurs when working with a pH > optimum pH) and of ozonation, for treating micropollutants (MP), in natural water. It was decided to work with five pharmaceuticals (carbamazepine, flumequine, ibuprofen, ofloxacin, sulfamethoxazole) selected as model micropollutants, and with natural water spiked with the microcontaminants under examination (initial concentration fixed to $15\mu\text{g L}^{-1}$ for each contaminant) as model effluent. So, it was possible to operate photo-Fenton under mild conditions since the purpose was to eliminate low concentrations of contaminants.

In general, the reaction rates are slow due to the originally low concentrations of the microcontaminants; in fact degradation of pollutants at low concentrations by AOPs follows pseudo-first-order kinetics ($r=k_{ap}C$). Therefore, one of the solutions for increasing process efficiency would be to increase C_0 . Under these conditions the combination of AOPs with membrane processes has attracted attention during the last few years, as the concentrations in retentates would be much higher than in raw WWTP effluents. So it was decided to perform the above mentioned AOPs in combination with a nanofiltration (NF) process. Pharmaceuticals dissolved in water were concentrated by NF, discharging a permeate free of contaminants. The retentate was then recirculated until the desired pre-concentration was achieved. The concentrate was treated with solar photo-Fenton, mild photo-Fenton with EDDS complex and ozonation and compared to direct AOP treatment carried out with natural water spiked with different $\mu\text{g L}^{-1}$ concentrations (15 to $150\mu\text{g L}^{-1}$, equal to the ones expected at the end of NF for different concentration factors, CF) of five different micropollutants. All the experiments were carried out with natural water as the intention was not only to evaluate the effect of pre-concentration of micropollutants and salts, obtained by a NF process, on the three different AOPs (AOPs kinetics and H_2O_2 , EDDS, O_3 consumption) discussed in this job but also to properly determine the pharmaceuticals and ions retention on the NF membranes depending on the operating conditions without the problems associated with WWTP effluents. In fact, using real effluents that usually contain solids and organics produced in the secondary treatment that could disturb analytical techniques for determining MP and could damage NF (since we didn't know how would be the membranes behavior), a proper pre-treatment would be necessary.

Then, only in the case of mild photo-Fenton with EDDS complex and ozonation, the experiments were performed with and without carbonate species in order to evaluate their influence too, since they are known as $\bullet\text{OH}$ radical scavengers. In the case of mild photo-Fenton carbonates were always removed because their removal has been shown to be necessary for high enough efficiency when operating photo-Fenton under mild conditions.

Hydrogen peroxide consumption and pharmaceutical removal rates were the key parameters for comparing results.

Results and discussion

-Nanofiltration experiments

The preliminary experiments showed that the NF90 (FILMTEC Membranes) membranes used in this study show very high multivalent and monovalent ion rejection rates (>70%) and as the concentration factors (CF) tested in the NF pilot plant were 4 and 10, pre-concentration of ions was very important

Again it was possible to note that permeate and concentrate flows, as well as pressure before and after the membranes, varied during operation. Evolution of trans-membrane pressure and decrease in permeate flow were more relevant when CF was 10, but did not affect pharmaceutical retention.

The membrane autopsy showed that cation calcium Ca^{2+} (due to its precipitation on the NF membrane surface as CaCO_3) strongly contributed to membrane scaling (scaling is due to the presence in the feed matrix of slightly soluble compounds as carbonates, hydroxides, sulfates, sulfides, fluorides, phosphates which may precipitate on the membrane as a result of the permeation process). Again, concerning the adsorbed foulness which causes the scaling and consequently the failure of the membrane, the autopsy has proved that the most efficient technique is the cleaning with the acid solution. In conclusion, in order to lengthen the useful life of the membranes, it would be better to conduct a specific future study concerning the most proper dosage of the acid solution to use which allows to reduce the membrane fouling and which, at the same time, avoids damaging the membrane (in fact, also an excessive use of acid solution may damage the membrane).

-Solar mild photo-Fenton experiments

By preliminary experiments, it was very clear that by increasing the starting concentration, process efficiency increases with initial reaction rate but until the first order kinetic reaches a point from which even if the initial concentration increases the initial rate does not increase significantly. This can be observed in the plot of r_0 vs. ΣC_0 , in *Figure 1*, which shows a linear trend up to a ΣC_0 value of about $750 \mu\text{g L}^{-1}$ (which corresponds to a CF 10). This result revealed that it was not recommendable to concentrate over a CF 10 because it would not have led to a considerable increase in initial reaction rate that could justify the effort in concentrate over a CF 10 and also to take into account the membranes operations.

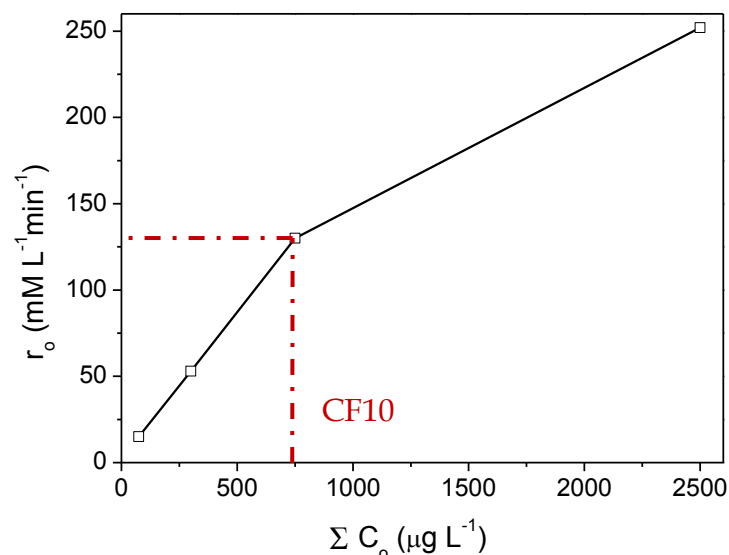


Figure 1. The plot of r_o vs. ΣC_o , where ΣC_o is the sum ($\Sigma C_o = 75, 300, 750$ and $2500 \mu\text{g L}^{-1}$) of the five selected micropollutants at the same starting concentration ($C_o = 15, 60, 150$ and $500 \mu\text{g L}^{-1}$).

The solar mild photo-Fenton experiments at different C_o showed the following results:

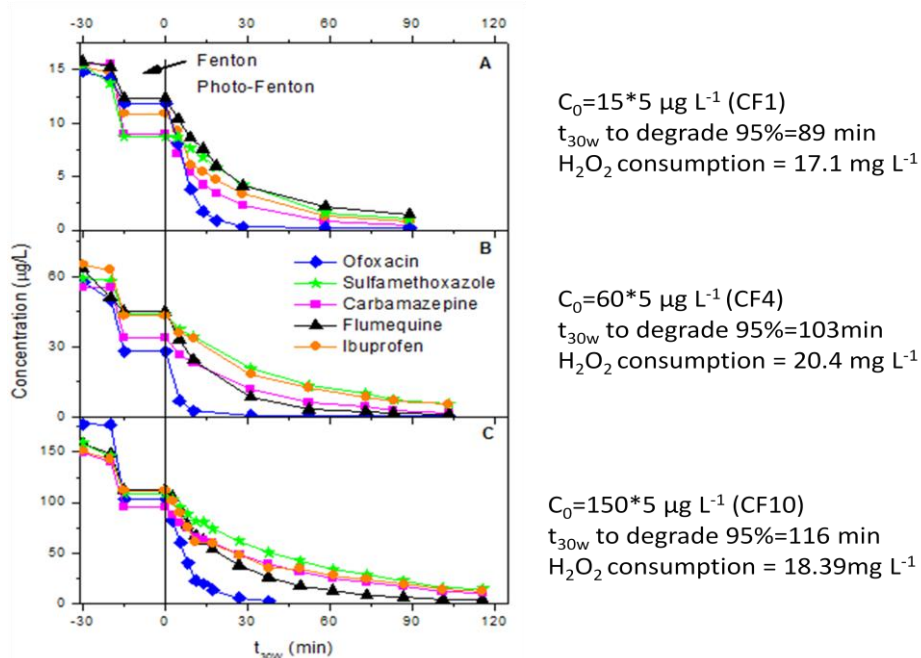


Figure 2. Mild photo-Fenton treatment without NF. Pharmaceuticals concentrations vs. time, for initial concentrations (C_o) of $15 \mu\text{g L}^{-1}$ (A), $60 \mu\text{g L}^{-1}$ (B) and $150 \mu\text{g L}^{-1}$ (C) for each micropollutant. Comments on the results are shown too.

While the results obtained by the NF/solar mild photo-Fenton experiments at different CF are:

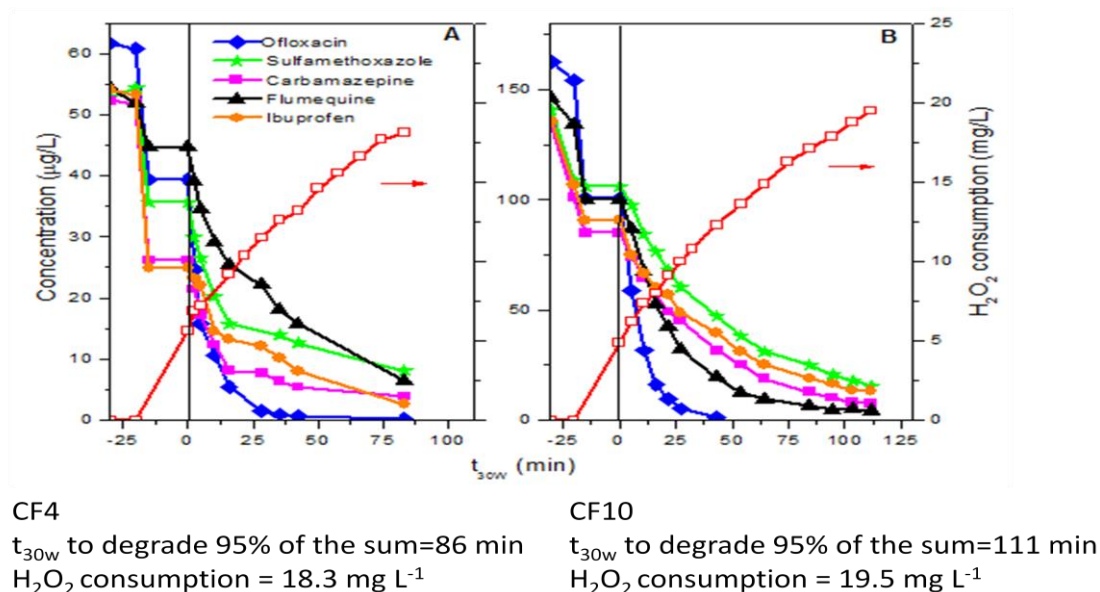


Figure 3. *NF/mild photo-Fenton. Pharmaceuticals concentrations vs. time and hydrogen peroxide consumption (red line) for CF=4 (A) and CF=10 (B). Comments on the results are shown too.*

All the results obtained and also the results reported by others authors confirm that the photo-Fenton performed in mild conditions ($\text{pH } 5\text{-}6$, $5 \text{ mg L}^{-1} \text{ Fe}^{2+}$ and $25 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$) to remove micropollutants, as tertiary treatment, is a very efficient process. Besides, in combination with NF, better results were obtained in terms of H_2O_2 consumptions and degradation times even taking into account that concentrating implies that a smaller volume (which decreases when CF increases) had to be treated with the AOP and a clear effluent (permeate) was produced (with a volume that increases when CF increases) and so a larger volume was possible to treat.

Additionally, H_2SO_4 dosage (g m^{-3}) needed for removing carbonates, decreased with the concentration factor, as only a part of the original carbonate concentration (feed matrix) was retained by the NF membranes, due to adsorption on surface membrane, and so the total carbonates in the retentate were lower than in the NF feed water.

Besides, it is important to note that in all the experiments, the total volume of treated water was the same, but in the case of NF/mild photo-Fenton experiments at CF=4 and CF=10, only 25% and 10%, respectively, of the total volume was finally treated by photo-Fenton, as the rest was NF permeate.

Consequently, since the amount of the main reagents needed to perform the mild photo-Fenton experiments (H_2SO_4 for carbonates removal and H_2O_2) refers to total volume of water to be treated, when using NF/photo-Fenton these reagents were used more efficiently.

- Solar mild photo-Fenton with EDDS complex experiments

The preliminary results showed that the complex (Fe(III):EDDS) is seriously affected by the presence of carbonate species (natural water) favouring the breakage of the complex, the subsequent iron precipitation and making the process less effective.

Then, the results of NF/mild photo-Fenton with EDDS at different CF (CF4 and CF10) experiments and the results of the mild photo-Fenton with EDDS at $\Sigma\text{C}_0=15*5 \mu\text{g L}^{-1}$ experiment, in both cases without carbonates, are presented below:

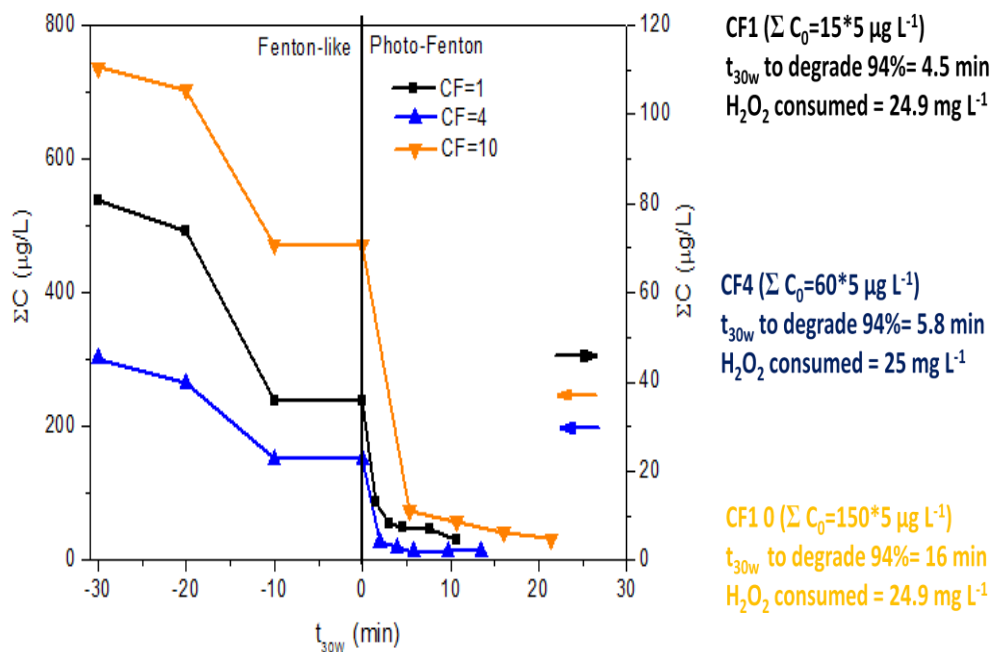


Figure 4. Degradation of the sum of the five selected micropollutants through photo-Fenton with EDDS complex without carbonate species for $\text{CF}=1$ ($\Sigma\text{C}_0=15 \times 5 \mu\text{g L}^{-1}$), $\text{CF}=4$ ($\Sigma\text{C}_0=60 \times 5 \mu\text{g L}^{-1}$) and $\text{CF}=10$ ($\Sigma\text{C}_0=150 \times 5 \mu\text{g L}^{-1}$). The comments on the results are shown too.

Also for these experiments, H_2SO_4 (g m^{-3}) needed for removing carbonates decreased with the concentration factor, as for the mild photo-Fenton experiments. As already said, the total volume of treated water was the same, but in the case of NF/mild photo-Fenton with EDDS

experiments at CF=4 and CF=10, only 25% and 10%, respectively, of the total volume was finally treated by photo-Fenton, as the rest was NF permeate.

Consequently, since the amount of the main reagents needed to perform the mild photo-Fenton with EDDS experiments (H_2SO_4 for carbonates removal, H_2O_2 and EDDS) refers to total volume of water to be treated, when using NF/mild photo-Fenton with EDDS these reagents were used more efficiently. Finally, also in this case is possible to remark that concentrating implies that a smaller volume (which decreases when CF increases) had to be treated with the AOP and a clear effluent (permeate) was produced (with a volume that increases when CF increases) and so a larger volume was possible to treat.

-Ozonation experiments

The following figure shows the results of NF/O₃ experiments at different CF (CF4 and CF10), with and without carbonates:

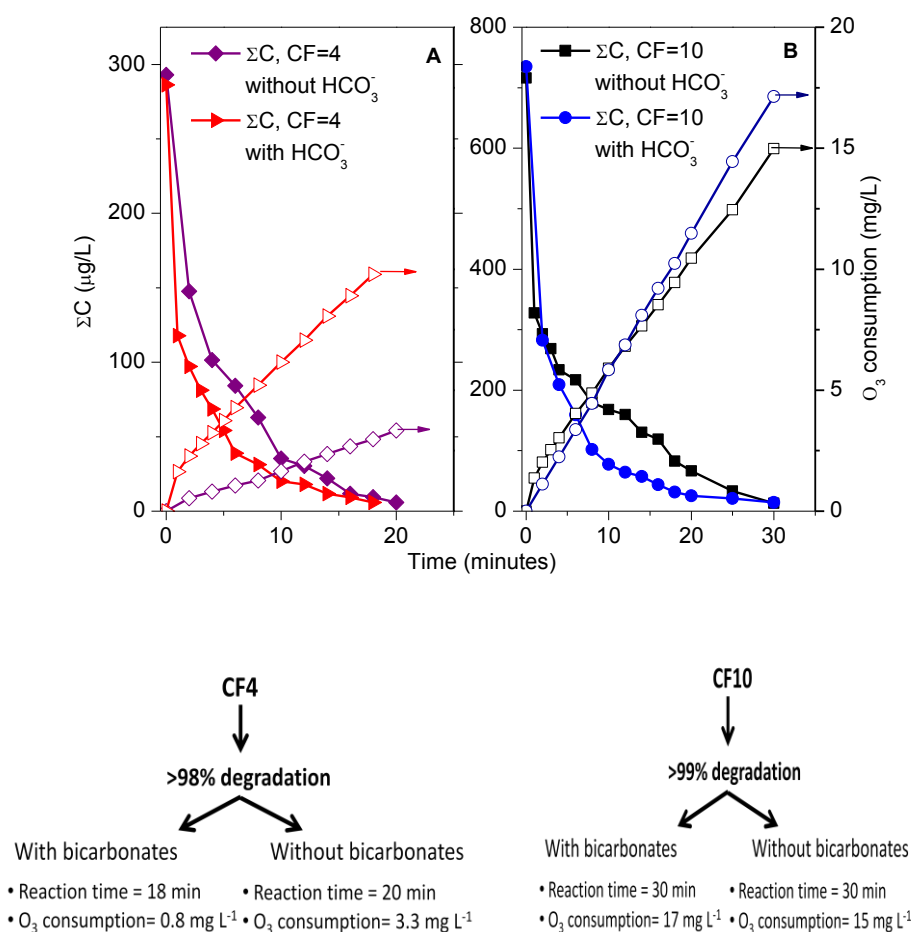


Figure 5. Profile of degradation of the five micropollutants sum (ΣC) with and without HCO_3^- for CF=4 (A) and for CF=10 (B) and comments on the results.

Finally the assay, carried out without using NF (CF=1) at $\Sigma C_0 = 15 \cdot 5 \mu\text{g L}^{-1}$ and with and without bicarbonates showed a reaction rate and an ozone consumption approximately the same as those observed in the assays with a CF=4 and CF=10, while the salts concentrations in water were lower.

The results presented above showed that it was better to work with bicarbonate avoiding any pretreatment of the water although the ozone consumption was higher. In fact, the results of degradation times were the approximately the same in all experiments so that there was not a substantial improvement in the fact of working without bicarbonates.

Finally, also in this case concentrating implies that a smaller volume (which decreases when CF increases) had to be treated with the AOP and a clear effluent (permeate) was produced (with a volume that increases when CF increases) and so a larger volume was possible to treat.

-Toxicity tests

In the cases where NF was not applied toxicity did not change significantly, the inhibition was always less than 15%. Also in the NF/mild photo-Fenton and NF/mild photo-Fenton with EDDS experiments the values of inhibition did not change significantly between CF=4 and CF=10 but they were a bit higher, especially 28-35% in the first case and 21-35% in the second case, but still no toxic, since the acute toxicity is expressed as the concentration of a compound which produces a 50% reduction in the initial bioluminescence of the bacteria.

Also the effluents treated by the means of ozonation showed inhibition values around 10-15% which again confirmed that there was no relevant toxicity.

Conclusions

Nanofiltration experiments

- By preliminary experiments the most efficient technique to avoid the scaling membrane was proved to be the cleaning with the acid solution but a specific future study is required to find out the most proper dosage of the acid solution to use, with the aim to reduce the membrane fouling and, at the same time, avoid damaging membrane

Solar mild photo-Fenton experiments

- Concentrating contaminants by NF produced a clean effluent (the permeate), which means that a larger volume was treated, and a concentrated stream. By applying mild

photo-Fenton to this stream, hydrogen peroxide consumption and treatment time were both reduced. Less H₂SO₄ was needed for carbonates removal.

Solar mild photo-Fenton with EDDS complex experiments

- It allowed to work with neutral pH and to obtain much lower degradation times comparable with typical degradation times of ozonation but avoiding an excessive increase of hydrogen peroxide consumption

Ozonation experiments

- Concentrating contaminants by NF produced a clean effluent (the permeate) , which means that a larger volume was treated, and a concentrated stream. It was better to work with bicarbonate avoiding any pretreatment of the water although the ozone consumption was higher, since the results of degradation times were approximately the same in all experiments.

Toxicity tests

- The treatments under examination didn't lead to toxic intermediates

The treatment of the concentrate, obtained through the previous NF process, by applying the AOPs under examination was consistent in any case and the reagents consumed were lower. So, a specific future economic study should be carried out in order to find out the better of the three AOPs discussed in this study, to treat a concentrate obtained by NF