Mixtures of chelating agents to enhance photo-Fenton process at natural pH: Influence of wastewater matrix on micropollutant removal and bacterial inactivation

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HIGHLIGHTS

- Mixtures of fertilizers as complexing agents are effective in photo-Fenton process.
- Process efficiency improvements are observed with organic fertilizers mixtures.
- More than 70% of micropollutants abatement is achieved in MBR matrix with mixtures.
- Higher iron release is observed in CAS matrix decreasing the process efficiency.
- Suitability of treated effluents for their reuse in agriculture is reached.

GRAPHICAL ABSTRACT
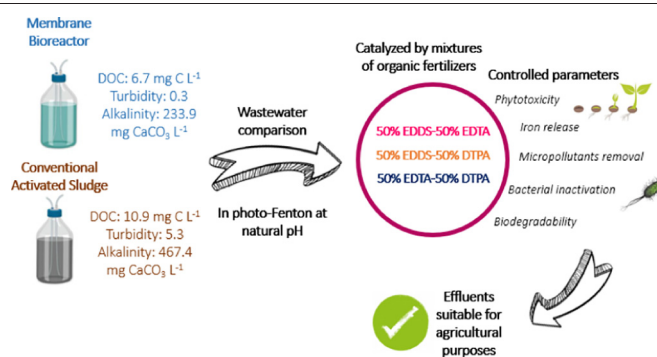
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ABSTRACT

Three organic fertilizers (EDTA (**Ethylenedinitrilotetraacetic acid**), EDDS (Ethylenediamine-N, N′-disuccinic acid) and DTPA (Diethylene triamine pentaacetic acid)) were tested as Fe-complexes in photo-Fenton process at natural pH for micropollutants (MPs) abatement and simultaneous *E.coli* inactivation. Less stable Fe-complexes show high iron precipitation, stopping MPs degradation. On the contrary, stable Fe-complexes imply low kinetic rates for MPs removal. To solve these inconveniences, three mixtures of organic fertilizers were also tested, trying to improve the kinetic rates of micropollutants oxidation and overcome iron precipitation. Three different pollutants (propranolol (PROP), acetamiprid (ACMP) and sulfamethoxazole (SMX)) were used as the target compounds. As the iron release is, in part, linked to the hardness of water, two water matrices from two different secondary wastewaters (Membrane Bioreactor (MBR) and Conventional Activated Sludge (CAS)) were tested. The best performance in micropollutant degradation and *E.coli* inactivation was achieved with the combination of EDDS + EDTA, accomplishing a good equilibrium between iron precipitation and rate of MPs removal. For instance, total removal of propranolol was achieved at 45 min in MBR, while it was only 85.7% in CAS, being an improvement of the process comparing with that obtained using single organic fertilizers. At the end of the treatment, 2.1 log-inactivation for *E.coli* was reached in CAS. The differences observed between both wastewaters were related to CAS' higher DOC, turbidity, and hardness. Finally, from the physicochemical characterization conducted, including Biochemical Oxygen Demand at 5 days and phytotoxicity, it is possible to highlight the suitability of these treated effluents for its reuse in irrigation, as long as in CAS matrix the final values of *E. coli* are within the legal limit.

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1. Introduction

The rapid growth of the population has caused fast global socio-economic changes, involving important environmental problems, such as water scarcity (Iglesias et al., 2007). At the current water consumption rate, in 2025 two-thirds of the world population could face water shortage, according to estimations of the World Wildlife Fund (WWF) (Ortega-Gómez et al., 2014). In front of this scenario, the development of suitable water reuse technologies is fundamental to confront water scarcity. The reuse of wastewater (WW) seems a good strategy for an efficient use of water, crucial for a sustainable development. In accordance with UNESCO (The United Nations Educational, Scientific and Cultural Organization), the agricultural sector represents about 70% of the total fresh water demand. The use of treated wastewater in this sector could guarantee agricultural production, mainly in areas with water deficit, reducing the water footprint. Nevertheless, the reuse of wastewater must negatively impact the public health. Thus, Regulation of the European Parliament and of the Council on minimum requirements for water reuse (European Commission, 2020) establishes the key parameters to be controlled for the agricultural reuse, such as *E. coli*. Conventional methods used for wastewater disinfection are based on chlorinated compounds (Iglesias et al., 2007; Nahim-Granados et al., 2019; Lima Perini et al., 2018). However, the formation of unhealthy and toxic substances, like halogenated disinfection by-products (DBPs), results to be dangerous for aquatic ecosystems and human health (Meireles et al., 2016). Sometimes it can be hard to simultaneously meet the limit for *E. coli* and residual chlorine ($< 1 \ mg \ L^{-1}$), making impossible the reuse of wastewater treated in this way for agricultural purposes (Nahim-Granados et al., 2019; ISO-16075-2). Consequently, the evaluation of less conventional technologies has gained importance in the last decades. Different studies have proven the efficiency of homogeneous Advanced Oxidation Processes (AOPs) on bacterial inactivation (Fiorentino et al., 2019; Malvestiti et al., 2019a; Malvestiti et al., 2019b) and micropollutants (MPs) abatement (Rodríguez-Chueca et al., 2018; López et al., 2018; Cruz-Alcalde et al., 2020). Additionally, studies with iron-based materials in heterogeneous AOPs suggested that these can play an important role in a large-scale wastewater treatment (Luo et al., 2021). Among AOPs, the use of solar driven processes seems a good strategy, being an ecofriendly option, which allow important reductions of electric costs. In this sense, solar photo-Fenton has gained importance among these alternatives due to its capabilities for water purification (Soriano-Molina et al., 2021; Ahile et al., 2021; López-Vinent et al., 2019). However, the required acidic conditions for photo-Fenton constitute the most serious drawback for its full-scale application (López-Vinent et al., 2020a). In that case, some authors proposed different chelating agents to work at natural pH. EDTA (**Ethylenedinitrilotetraacetic acid**), EDDS (Ethylenediamine-N, N′-disuccinic acid), citric acid and oxalic acid are, among others, the most investigated compounds (Huang et al., 2012; García-Fernández et al., 2019; Miralles-Cuevas et al., 2014; de Luca et al., 2014). Recently, organic fertilizers such as DTPA (Diethylene triamine pentaacetic acid) (López-Vinent et al., 2020b) and EDDHA (Ethylenediamine-*N,N′*-bis(2-hydroxyphenylacetic acid)) (Nahim-Granados et al., 2019) were also studied as the chelating agents to perform photo-Fenton process at natural pH.

As observed in previous studies, EDDS displays low stability with iron, which results in higher kinetic rates of MPs degradation at the first minutes of the treatment. Then, the efficiency decreases presenting a plateau and failing to reach the complete MPs removal (López-Vinent et al., 2020a, 2020b). However, other chelating agents, like DTPA, which presents high stability with iron, shows low kinetic rates in MPs abatement. However, in such case, continuous MPs degradation was observed, achieving good removals at the end of the treatment. In a previous work, the behavior of EDDS, EDTA and DTPA was studied in different wastewater effluents (López-Vinent et al., 2020b) and was discussed regarding the evolution of iron during the experiment.

These results displayed the necessity to search for chelating agents whose use could avoid high iron precipitation and lead to fast kinetic rates in MPs degradation. For this reason, mixtures of EDDS, EDTA and DTPA were used in this study. These combinations should lead to a mix of both unstable iron complexes providing high rates for MPs removal and iron-stable complexes allowing the continuous formation of hydroxyl radical, thus avoiding the efficiency decrease. Furthermore, these combinations could prevent additional treatments to remove iron hydroxides, because of a lower iron precipitation compared to that observed in treatments using EDDS only. Moreover, the treatment time should decrease compared to that in treatments employing more stables iron chelates. Another advantage is related to the reuse of wastewater for agricultural purposes: all three chelating agents are fertilizers approved by the European Commission (European Commission, 2003).

Different type of wastewaters effluents can be found in WWTPs due to different treatments and wastewaters used. The physicochemical parameters of wastewater greatly influence the efficiency of micropollutants abatement with AOPs (López-Vinent et al., 2020a, 2020b; Maniakova et al., 2021). The turbidity, DOC and alkalinity can affect the photo-chemical reactions due to light scattering, competition for hydroxyl radicals due to the organic matter present in the matrix and hydroxyl radicals scavenging due to the presence of carbonate and bicarbonate.

Summarizing and according all the commented in the last paragraphs, the aim of this study is to evaluate the efficiency of organic fertilizers mixtures on micropollutants abatement and *E.coli* inactivation by photo-Fenton at natural pH, in two different wastewaters. Three micropollutants were selected as model compounds: propranolol hydrochloride (PROP), acetamiprid (ACMP) and sulfamethoxazole (SMX). The selected matrices correspond to two secondary effluents, from membrane bioreactor (MBR) and Conventional Activated Sludge (CAS) treatments with distinct physicochemical characteristics, especially in organic matter, turbidity, and alkalinity. The performance of organic fertilizers mixtures will be compared to single compounds usage, being one of the main goals, along with wastewater comparison to determine the role of WW properties on iron precipitation and subsequent slowdown of degradation kinetics. Linked to this, another endpoint in this work is to identify the organic fertilizers combinations which are more suitable for each type of wastewater and relate it to their relative stability with iron. Finally, the feasibility of reusing these treated effluents for agricultural purposes was assessed through Biochemical Oxygen Demand (BOD_5) analyses. The results of each condition at the end of the treatment were compared with the maximum limit in the legislation for its reuse. Additionally, phytotoxicity was evaluated during the treatment by *E.sativa* seeds.

2. Material and methods

2.1. Chemicals

Three micropollutants were selected as model compounds: propranolol hydrochloride (PROP), acetamiprid (ACMP) and sulfamethoxazole (SMX), all of them acquired from Sigma-Aldrich. EDDS-Na solution (purchased from Sigma-Aldrich), DTPA-Fe (7% of iron) and EDTA-Fe (13.3% of iron), both obtained from Phygenera (Germany), were selected as chelating agents for photo-Fenton experiments. Catalase from bovine liver and Chormocult® Coliform Agar were acquired from Sigma-Aldrich. Hydrogen peroxide (H_2O_2, 30% w/v), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), orthophosphoric acid and acetonitrile were purchased from Panreac Química.

2.2. Wastewater matrices

Two secondary effluents from two different wastewater treatment plants (WWTPs) located in Barcelona (Spain) were selected to perform photo-Fenton experiments. They were collected from the outlet of a

Membrane Bioreactor and a Conventional Activated Sludge. They present markedly different physicochemical characteristics (see Table 1) mainly related to TOC (total organic carbon) and turbidity, which are expected to have an impact in photochemical experiments.

2.3. Photo-Fenton at natural pH experiments

A solar simulator (Xenonterm-1500RF, CCI) equipped with a Xenon lamp (1.5 kW) was used to perform the photo-Fenton experiments. Irradiance was determined by o-nitrobenzaldehyde actinometry (De la Cruz et al., 2013) obtaining a value of 13.9 W m^{-2} in the wavelength range between 290 and 400 nm. A tubular photoreactor was placed inside of the simulator (25 cm length x 2 cm diameter). During the assays, the solution was continuously recirculated from the feeding tank (1 L) to the tubular photoreactor. The medium temperature was kept constant at 25° by means of a Haake C-40 bath. A schematic design can be found in the supplementary material (Fig. S1).

Total iron in solution was 5 mg L^{-1} (corresponding to the maximum concentration allowed for water irrigation) (Guidelines 600/R-12/618; Ayers and Westcot, 1985) so that an appropriate amount of EDTA-Fe or DTPA-Fe was added to corresponding wastewater, previously acclimated. The calculations were performed according to the percentage of iron chelated in each case (see Section 2.1). In the case of EDDS, this was first dissolved and then the iron (5 mg L^{-1}) added to ensure the chelation and avoid iron precipitation. A molar ratio (Chelating agent: Fe) of 1:1 was selected according to our previous study (López-Vinent et al., 2020b). To prepare the solution with mixtures of chelating agents, the same total iron in solution than that used in experiments with a single chelating agent was employed (5 mg L^{-1}). In that case, 50% of chelated iron was added from one chelating agent and 50% from the other. Three mixtures were tested: EDDS + EDTA, EDDS + DTPA and EDTA + DTPA. A concentration of 0.25 mg L^{-1} of each micropollutant (PROP, ACMP and SMX) was added to the solution. The selection of these MPs was devised due to different kinetic constant values for reactions with hydroxyl radical (k$_{PROP,HO}$ = 1.0·10^{10} M^{-1} s^{-1} (Benner et al., 2008) k$_{SMX,HO}$ = 5.5·10^9 M^{-1} s^{-1} (Huber et al., 2003), k$_{ACMP,HO}$ = 2.1·10^9 M^{-1} s^{-1} (Cruz-Alcalde et al., 2017)). Finally, just before the experiment started, a concentration of 50 mg L^{-1} of H$_2$O$_2$ was added. During the experiment, samples were continuously withdrawn, and the reaction was stopped with catalase (200 mg L^{-1}). To evaluate the total iron in solution, the samples were filtered with 0.20 μm syringe filters and ascorbic acid in excess was added to the sample to reduce iron (III) to iron (II), which then reacts with o-phenanthroline.

All plots were performed considering the accumulated energy (Q$_{acc}$, kJ L^{-1}), calculated according to Eq. (1) (Romero Olarte, 2015).

$$Q_{acc} = \sum_{i=1}^{n} \frac{I \cdot \Delta t_i}{V} \tag{1}$$

where I is the irradiation entering the photoreactor (kJ s^{-1}), Δt$_i$ is the increment in the time of reaction (s) and V is the reaction volume (L).

2.4. Analytical techniques

High Performance Liquid Chromatography (Agilent Technologies) was used to measure the concentrations of all three micropollutants (PROP, ACMP and SMX). An isocratic method was employed for simultaneous MPs detection with a C-18 column (Tecknokroma, 200 × 4.6 mm i.d; 5 μm particle size). The wavelengths were fixed at 214, 250 and 270 nm for PROP, ACMP and SMX, respectively. The mobile phases selected were acetonitrile and water acidified with orthophosphoric acid (pH = 3) (20:80, respectively). The flux was set to 1 mL min^{-1} and an injection volume of 100 μL was used. Hydrogen peroxide (H$_2$O$_2$) concentrations were followed during the reaction by the metavanadate colorimetric method (Pupo Nogueira et al., 2005). Total dissolved iron was also monitored by the o-phenanthroline procedure (ISO 6332). The BOD$_5$ analyses were performed following the 5210-standard method (detection limit 1 mg O$_2$ L^{-1}). Seeds of *Eruca sativa* (arugula) were employed to determine the phytotoxicity (Tam and Tiquia, 1994) (further information can be found in the supplementary material Table S1). To perform the disinfection tests, 1 mL of each sample was plated on Chromocult® Coliform Agar (*E. coli* selective agar). Buffered peptone was used when dilution was needed. The plates were incubated at 35 °C for 24, 48 and 72 h. The standard plated count method was used to determine the colony-forming units per 1 mL (CFU mL^{-1}).

3. Results and discussion

3.1. Comparison of chelating agents' mixtures in two different wastewaters

Chelating agents have different efficiencies on MPs removal and bacterial inactivation due to their different chemical structure, which implies distinct stability constants with iron. In general terms, a low stability of iron chelates causes a fast abatement of MPs but, at the same time, quick iron precipitation causing a decrease in the process efficiency. Nevertheless, in the case of iron chelates with a higher stability, the opposite happens resulting in a low but continued rate of MPs removal (López-Vinent et al., 2020b). Thus, an equilibrium between high degradation rates and low iron precipitation is necessary for the process to be efficient.

Despite this, the performance on MPs abatement and bacterial inactivation are related to the complexity of the effluent. For these reasons, it is important to study the process with effluents presenting different physicochemical parameters to have a global vision of the process behavior in different systems. To study this influence, the process performance on two different WWTPs effluents, CAS and MBR, was compared in this work.

With the aim of comparing the efficiency of two wastewater matrices, the same combinations of chelating agents and concentrations of reagents were used (5 mg L^{-1} of iron and 50 mg L^{-1} of H$_2$O$_2$). Fig. 1 displays the degradation curves of PROP (a), ACMP (b) and SMX (c) catalyzed by the combination of 50% EDDS +50% EDTA in both secondary effluents (MBR and CAS). In addition, the removals of three MPs using 100% EDDS and 100% EDTA were also plotted. The pH evolution was followed during each experiment. Only variations of ±0.2 were observed since real and naturally buffered wastewater effluents were employed.

As can be observed in Fig. 1, the best removal was observed for PROP and the worst for ACMP, in all cases. With MBR effluent, similar to CAS, the trend of all three MPs was the same regardless of the employed iron chelates (see Fig. 1a, 1b and 1c). The most representative difference was observed for ACMP during the first 60 min (0.77 kJ L^{-1}). For instance, with the EDDS-EDTA mixture, the degradation of ACMP was 60.9% at 60 min, while with EDDS and EDTA the removals were 39.4 and 32.9%, respectively. This fact is related to the low kinetic rate constant of reaction between hydroxyl radicals and ACMP, so that the MPs removals
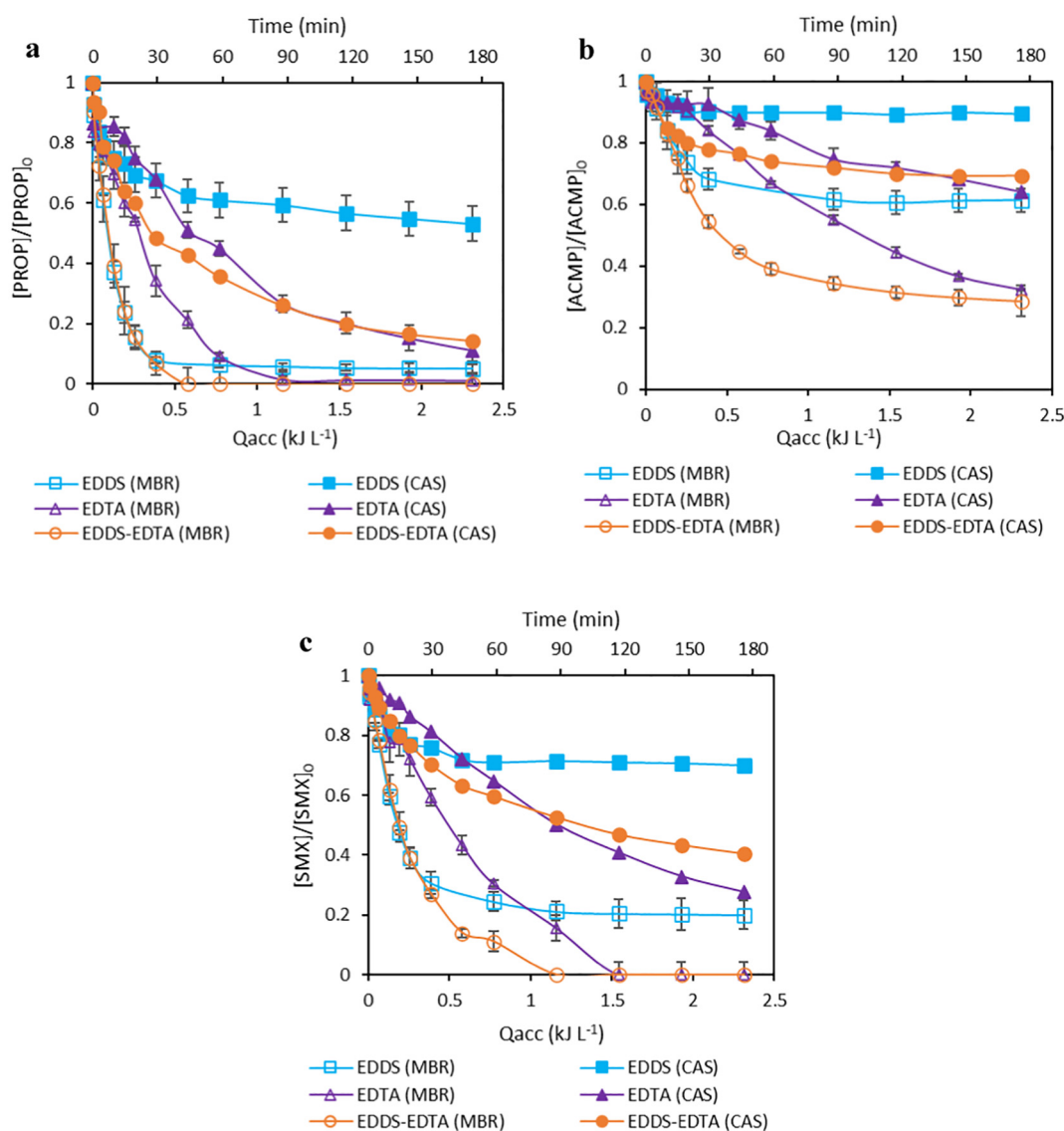
Table 1
Principal parameters of two wastewaters characterization. N/A: below the detection level.

Parameters	MBR	CAS
pH	7.8	8.2
Turbidity (NTU)	0.3	5.3
UV$_{254}$ (m^{-1})	19.1	28.8
TOC (mg C L^{-1})	7.0	16.6
DOC (mg C L^{-1})	6.7	10.9
Total alkalinity (mg CaCO$_3$ L^{-1})	233.2	467.4
Cl^{-1} (mg L^{-1})	591.6	406.4
SO$_4^{2-}$ (mg L^{-1})	168.8	206
N-NO$_2^-$ (mg L^{-1})	0.4	0.4
N-NO$_3^-$ (mg L^{-1})	N/A	1.6

Fig. 1. Profile of a) PROP b) ACMP and c) SMX degradation as a function of the accumulated energy for photo-Fenton experiments at natural pH, with EDDS, EDTA and a mixture of both (50% EDDS +50% EDTA), in MBR (opened symbols) and CAS (closed symbols). $[PROP]_0 = [ACMP]_0 = [SMX]_0 = 0.25$ mg L^{-1}; $[Fe]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}.

were slower and an improvement in degradation with the combination is more noticeable.

The degradations at the end of the treatment with CAS were lower than those achieved in MBR, due to the higher complexity of the first matrix including a higher organic load. Thus, 100% of PROP abatement (with EDDS + EDTA) was reached in only 45 min (0.58 kJ L^{-1}) in the MBR matrix, whereas only 85.7% of PROP removal was observed at the end of the treatment (180 min, 2.31 kJ L^{-1}) in CAS matrix. This confirmed the competition for HO· and probably light scattering due to high organic matter and turbidity in CAS. This fact was already observed when EDDS and EDTA were used alone. Thus, the PROP degradation was 89.9% with EDDS and 65.8% with EDTA (Fig. 1a), at 0.39 kJ L^{-1} (30 min) in MBR. However, only 32.6% and 32.2% of PROP was removed in CAS for EDDS and EDTA, respectively. The higher organic load of the CAS effluent also explains that the difference in the degradation rates of PROP with EDDS and EDTA is larger in MBR compared to CAS, as oxidation of the organic load of that matrix can prevail over the degradation of the model pollutant.

Another key aspect to consider in the behavior of iron chelates as catalysts is the rate of iron precipitation. Fig. 2 shows the iron evolution during the photo-Fenton treatment with different organic fertilizers and

their mixtures in two wastewater effluents (Fig. 2a for MBR and Fig. 2b for CAS). EDDS quickly releases iron, while EDTA releases it more slowly. This fact can explain (see Fig. 1) that EDDS contributed to a higher reaction rate at the initial 30 min while EDTA participated in less iron precipitation throughout the reaction. In addition, the precipitation of iron in CAS was higher than that in MBR, mainly in the case of EDDS which forms the iron chelate with a lower stability. For instance, when EDDS was used, at 0.39 kJ L^{-1} (30 min) the iron precipitated was 81.5% in CAS and 38.7% in MBR (see Fig. 2). This behavior could be related to the highest complexity of CAS compared to MBR. The different compounds contained in wastewaters, such as ions, can be involved in the breakdown of the iron complex since they could perform new complexes with the complexing agent if the stability constant of the new combination is higher than that with iron. This fact results in a higher precipitation of iron in CAS than MBR. It constitutes another reason why the degradation of MPs at the beginning of the reaction was slower when EDDS was used in CAS.

Coming again to the combination EDDS + EDTA, in the case of MBR, the synergistic effect appears throughout the entire experiment. It should be noted that at the beginning of the experiment the behavior of this mixture is very similar to that with EDDS alone. However,
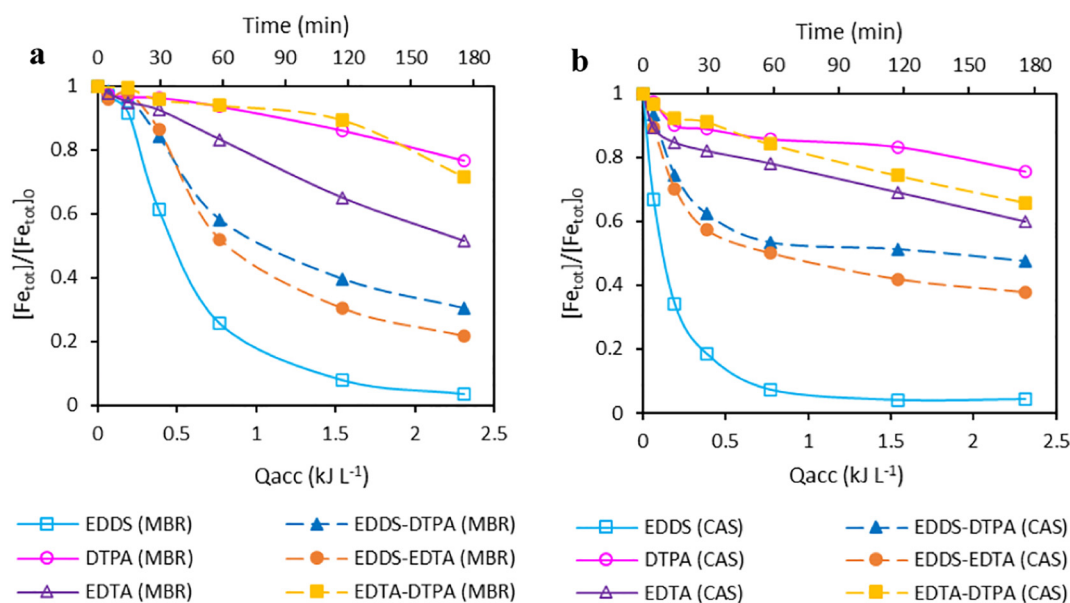
Fig. 2. Iron evolution during the experiment as a function of the accumulated energy for three chelating agents and their mixtures in photo-Fenton at natural pH in a) MBR and b) CAS. $[PROP]_0 = [ACMP]_0 = [SMX]_0 = 0.25$ mg L^{-1}; $[Fe]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}.

given the presence of EDTA as well, the plateau formed when EDDS alone is used appears much later in the case of EDDS + EDTA. This shows the good synergy between the release of iron by the EDDS, at the beginning of the experiment, and the minor but continuous release of iron throughout the whole experiment by EDTA. Therefore, the decrease in PROP concentration does not reach a plateau, as it would happen using only EDDS, but it continues to go down thanks to EDTA. All of this is also corroborated by the data in Fig. 2, which shows the evolution of the concentration of iron in solution throughout the experiment, as commented before. It can be seen that at the end of the experiment and thanks to EDTA, there is still a large amount of iron in solution which causes, as mentioned before, the plateau not to appear, and therefore PROP degradation continues. The evolution of H$_2$O$_2$ decomposition of different organic fertilizers and their mixtures is displayed in Fig. S2. In all cases, at the end of the experiment, not all the H$_2$O$_2$ was consumed. This fact evidences that the plateau observed for EDDS in MPs abatement was not caused by a lack of oxidant.

In the case of CAS, the EDDS + EDTA synergy is noticeable during the first half of the experiment and disappears towards the end, where even the use of EDTA alone offers better results than the EDDS + EDTA mixture. This could be explained because, in the case of CAS, there is a higher organic load that competes with the MPs for hydroxyl radicals. Thus, at the beginning, the effect of EDTA to avoid the EDDS plateau is noticed but, in turn, it causes a higher precipitation rate of the EDTA iron which explains that at the end of the experiment, the EDDS + EDTA mixture behaves worse than EDTA alone. As seen in Fig. 2, much less iron remains in solution at the end of the experiment for the EDDS + EDTA combination than for EDTA alone. This was also the case with MBR. However, in that assay the effect of EDDS is much more powerful and allows the PROP degradation to go a long way. With this, the supplementary effect of EDTA, even if it is less, already allowing the synergy to continue until the end of the experiment, achieving the total degradation of PROP.

In CAS matrix, the degradation of ACMP and SMX with different chelating agents followed the same trend than PROP (46.8% for EDDS, 88.8% for EDTA and 85.7% for EDDS-EDTA). ACMP achieved 10.4%, 35.8% and 30.6% and SMX presented 30%, 72.5% and 59.5% for EDDS, EDTA and the combination of both, respectively, at 180 min (2.31 kJ L^{-1}).

In CAS matrix, at the end of the treatment, EDTA and the mixture of both chelating agents presented similar results for all three MPs.

However, an enhancement in MPs degradation and dissolved iron was observed comparing EDDS with the combination of EDDS and EDTA. For instance, the degradation of PROP at the end of the treatment was 1.8 times higher and the precipitation of iron was 2 times lower with 50% EDDS +50% EDTA than those observed for EDDS. In addition, the application of the mixture (EDDS + EDTA) to the crops is a more sustainable measure since EDDS presents a biodegradable character and EDTA was more recalcitrant, negatively affecting the soils when the plants do not absorb all the amount of applied fertilizer (López-Rayo et al., 2016). Using the mixture, less EDTA would be poured to the ecosystems and similar MPs degradation and iron precipitation could be achieved.

For a better understanding of the effect of combining different chelating agent's, two more mixtures of were tested. Fig. 3 shows the degradation curves of three MPs catalyzed by 50% EDDS +50% DTPA, and Fig. 4 presents the results for 50% EDTA +50% DTPA.

As can be observed in Fig. 3a for CAS effluent, both the experiment with the combination of EDDS + DTPA and 100% EDDS presented overlapped curves until 0.39 kJ L^{-1} (30 min), while DTPA showed a slow kinetic rate. Then, the PROP degradation with EDDS stopped down due to the high iron precipitation, achieving only 46.8% abatement at the end of the treatment. Nevertheless, the removal of PROP with the combination of both chelating agents reached 60.4% of degradation, equal than the experiment using only DTPA. As commented for the mix EDDS + EDTA, the higher organic load of CAS competes with the MPs for hydroxyl radicals. Being so, at the beginning of the experiment, DTPA can avoid the EDDS plateau but, in turn, the precipitation rate of iron coming from DTPA increases, explaining that at the end of the experiment, the EDDS + DTPA mixture behaved similarly to DTPA alone. In addition, for the mixture EDDS + DTPA the iron remaining in solution was higher than that observed in the test using EDDS alone, and lower than in the test with DTPA alone (see Fig. 2b). Therefore, this can explain the fact that the degradation of MPs with EDDS + DTPA followed an intermediate behavior between EDDS and DTPA separately.

In the case of experiments with the MBR matrix, iron precipitation was slower reaching good MPs abatement kinetics during the first 30 min (0.39 kJ L^{-1}). This fact implies that the difference in MPs removal between EDDS and DTPA was higher in MBR compared to CAS. Thus, the effect of iron precipitation is much more important in effluents with higher DOC and alkalinity, due to faster precipitation as
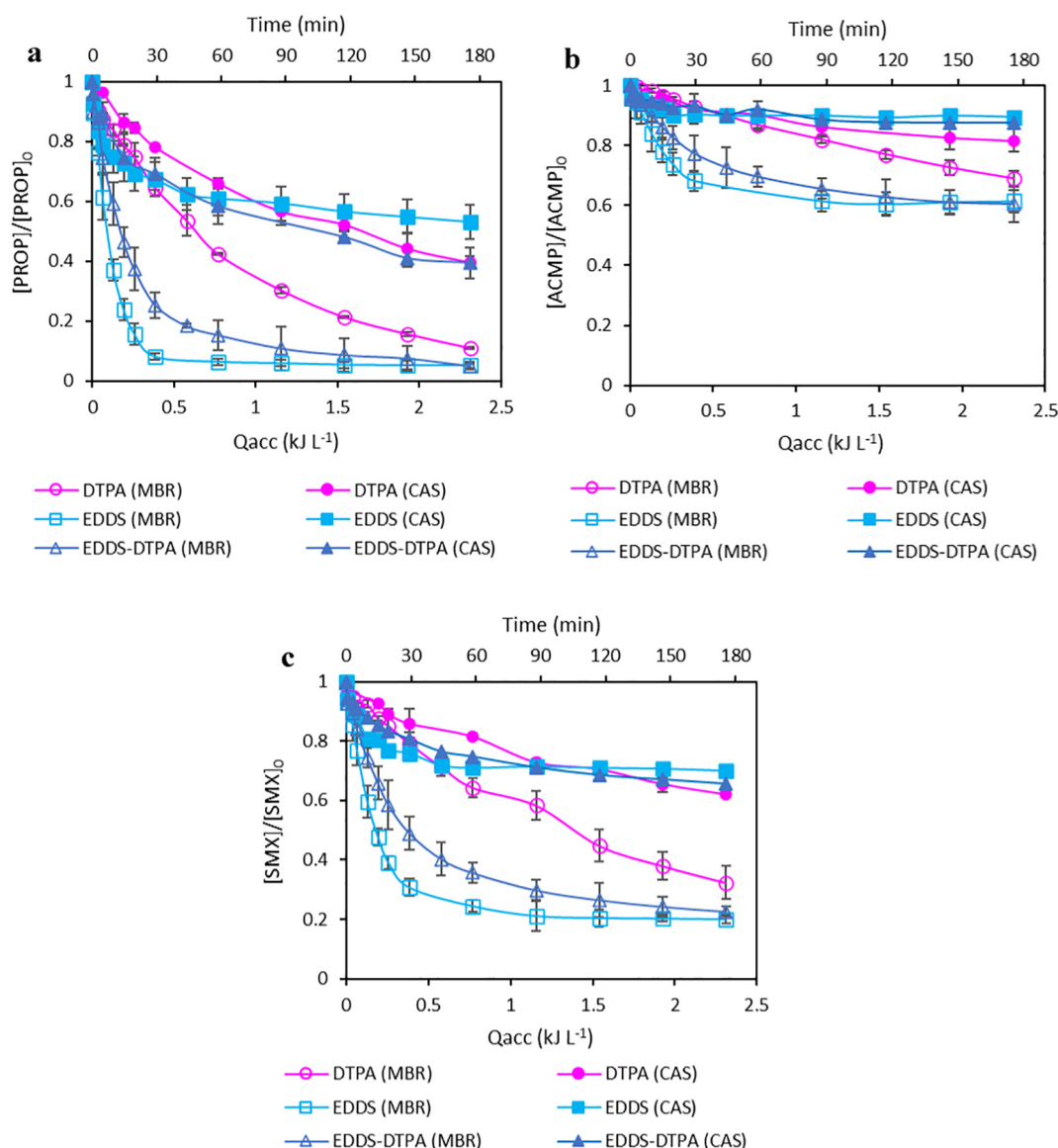
Fig. 3. Profile of a) PROP b) ACMP and c) SMX degradation as a function of the accumulated energy for experiments with EDDS, DTPA and a mixture of both (50% EDDS +50% DTPA) in photo-Fenton at natural pH in MBR (opened symbols) and CAS (closed symbols). $[PROP]_0 = [ACMP]_0 = [SMX]_0 = 0.25$ mg L^{-1}; $[Fe]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}.

commented before. However, DTPA did not achieve better removals than EDDS at 90 min (1.16 kJ L^{-1}), as happened in CAS effluent. The results for ACMP and SMX when the combination of two chelating agents was employed were: 12.4 and 34.4% in CAS and 39.4 and 77.4% in MBR, respectively.

Comparing the two mixtures performed with EDDS (i.e., EDDS + DTPA (Fig. 3) and EDDS + EDTA (Fig. 1)), it was noted that in the combination with EDTA better removals were achieved for all three MPs because both EDTA and EDDS presented higher degradation rates during the initial instants. This fact implies that the higher MPs degradation is produced before the iron precipitation was very pronounced. However, in the case of the EDDS + DTPA combination, the kinetic rates were slower, due to the fact that DTPA presents higher stability in its combination with iron. For this reason, the iron precipitation exerts a stronger effect when this mixture of chelates was tested because at 60 min (0.77 kJ L^{-1}) the iron in solution was about 50% in both effluents. This fact caused the reduction in the efficiency of the process, consequently failing to reach total MPs removal. The same fact was observed when 100% of EDDS was tested. At 0.39 kJ L^{-1}, the degradation of all three MPs was stopped due to the high iron precipitation. In addition, with

the EDDS-EDTA mixture this fact was also seen in ACMP, since this compound presents slower oxidation kinetics with hydroxyl radical. Thus, the removal was stopped at 0.77 kJ L^{-1}, when the iron precipitation was very high, and total degradation was not reached.

Fig. 4 displays the results obtained through the combination of 50% EDTA +50% DTPA for PROP (Fig. 4a), ACMP (Fig. 4b) and SMX (Fig. 4c) degradation in MBR and CAS effluents. The EDTA-DTPA chelates mixture allowed to reach similar degradation kinetics than EDTA alone, achieving the same PROP abatement (about 87% in CAS at 180 min and 100% at 90 min in MBR). EDTA + DTPA mixture improves the behavior of DTPA since only 60.5% of PROP removal was achieved with DTPA alone, at 180 min. The same fact happened with ACMP and SMX. In addition, in experiments using the combination EDTA-DTPA about 1.2 times less iron precipitated compared to tests with EDTA, which is better for the agricultural purposes as it avoids iron chlorosis in plants.

On the other hand, and comparing the mixtures of chelating agents tested, EDTA + DTPA (see Fig. 4) achieved better results than the combination EDDS + DTPA (see Fig. 3) in both effluents (MBR and CAS) at the end of the treatment (180 min). Until 0.6 kJ L^{-1} (45 min) the
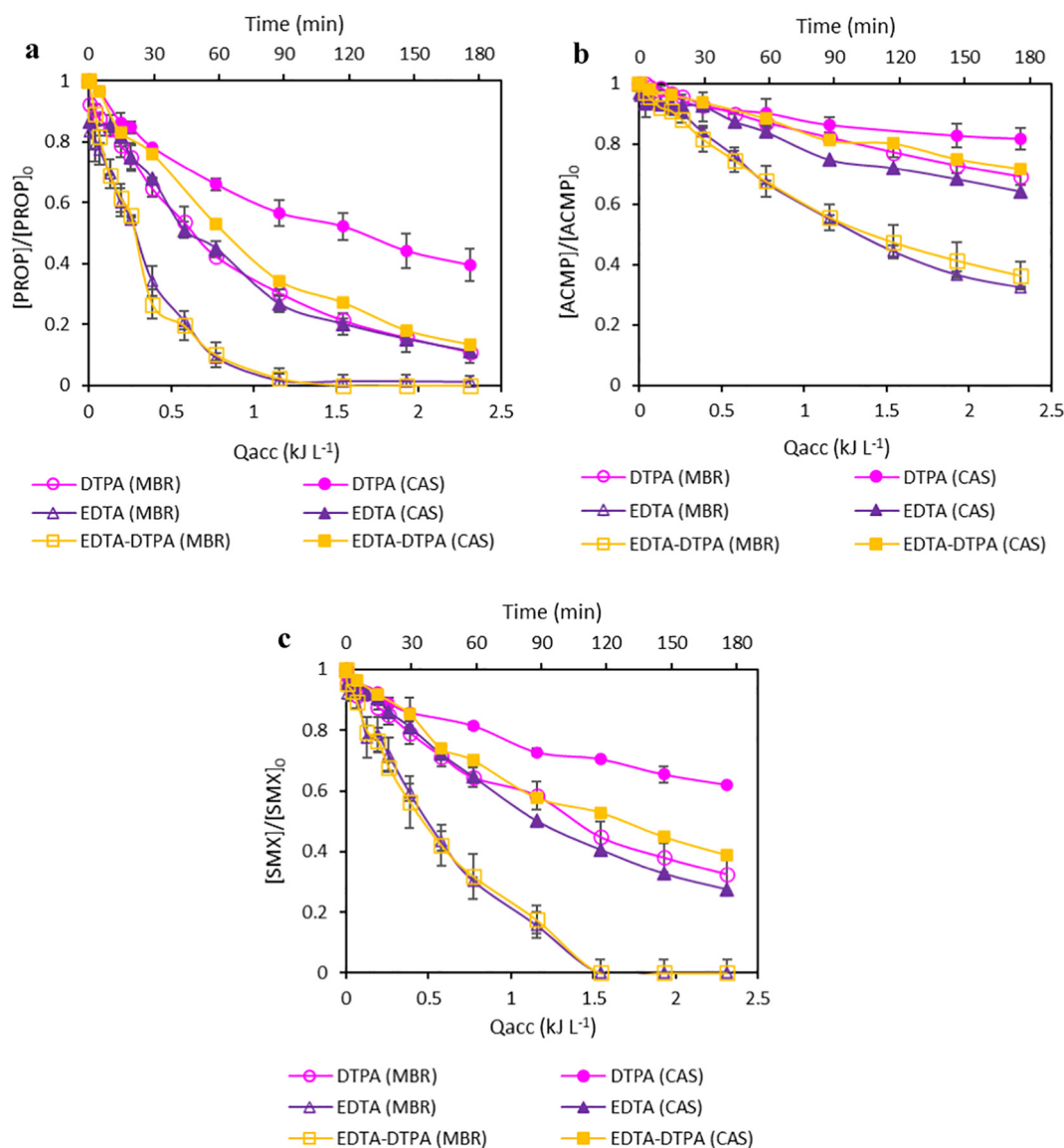
Fig. 4. Profile of a) PROP b) ACMP and c) SMX degradation as a function of the accumulated energy for experiments with EDTA, DTPA and a mixture of both (50% EDTA +50% DTPA) in photo-Fenton at natural pH in MBR (opened symbols) and CAS (closed symbols). $[PROP]_0 = [ACMP]_0 = [SMX]_0 = 0.25$ mg L^{-1}; $[Fe]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}.

degradations of all three MPs were similar in both effluents and chelating agent's combinations. Then, the mixture EDTA + DTPA presented higher removals in all the experiments. The reason is the higher iron precipitation when EDDS + DTPA was tested (approximately 2.5 times higher than EDTA + DTPA). The different behavior of the three mixtures of chelating agents can also be explained from this different rate of iron precipitation, similarly to the EDDS + EDTA mixture. Thus, EDTA and DTPA release iron in a more sustained way during the experiment, and not abruptly at the beginning and very slowly at the end as observed for EDDS. This would explain why the EDTA + DTPA mixture had better results than the EDDS + DTPA mixture, as DTPA releases iron very slowly and, at the end of the experiment, it cannot compensate the lack of iron caused by the fact that EDDS released it so quickly. In the case of the EDDS + EDTA combination, EDDS also releases iron very quickly but EDTA is capable to release it to a higher extent than DTPA. Therefore, ensuring that, at the end of the experiment, enough iron remains in solution allowing the continuity of the MPs degradation reactions. That is why the EDDS + EDTA mixture gave the best results.

3.2. Bacterial inactivation in Conventional Activated Sludge effluent

E.coli inactivation was also evaluated in CAS. Fig. 5 displays the inactivation curves corresponding to experiments employing the three chelating agents (EDDS, EDTA and DTPA) and their corresponding binary mixtures. The quantification of wild *E. coli* disclosed concentrations in the range of 10^3–10^4 colony-forming units per mL (CFU mL^{-1}) at initial time. Experiments with only hydrogen peroxide demonstrated that under darkness conditions disinfection does not occur. A photolysis test was also carried out, achieving only 0.2 log-inactivation at 180 min (2.31 kJ L^{-1}).

Regarding the experiments with different chelating agents, EDTA showed the worst results with inactivation levels of 1.3 log at the end of the experiment. EDDS presented a 1.8 log inactivation. The two combinations of chelating agents including EDDS (EDDS + EDTA and EDDS + DTPA) achieved the best inactivation: 2.1 log-inactivation. On its part, DTPA and the mixture EDTA + DTPA showed the same inactivation: 1.5 log. Total inactivation was not reached in any of the studied cases. However, no regrowth was observed in any case at 48 and 72 h.
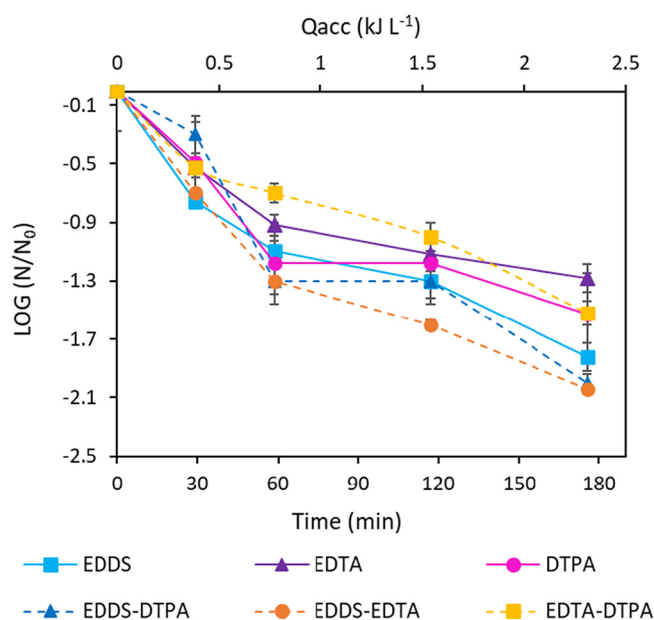
Fig. 5. *E. coli* inactivation in CAS with photo-Fenton process at natural pH catalyzed by DTPA, EDTA, EDDS and three different combinations of these chelating agents. $[Fe]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}.

Hydroxyl radicals formed in photo-Fenton at natural pH can affect proteins, lipids and DNA causing mortality in bacteria (Spuhler et al., 2010; García-Fernández et al., 2012). Moreover, intracellular diffusion of Fe (II) can generate internal Fenton reactions and also produce the inactivation of bacteria (Halliwell and Gutterridge, 1984; Polo-López et al., 2013). Nevertheless, in photo-Fenton at natural pH with high concentrations of iron (10 mg L^{-1}) the presence of Fe (II) is almost negligible, as observed in a previous work. In that case, the formation of oxyhydroxides was very fast and experiments with EDDS, which presented high iron precipitation, achieved worst inactivation results (López-Vinent et al., 2020b). However, in the present study combinations of EDDS with two other chelating agents allowed to reach the best log-inactivation. In this case, however, the initial iron concentration was lower and the formation of oxyhydroxides consequently slower, thus favoring the inactivation of bacteria. In addition, the MPs degradation kinetics and the inactivation rate of bacteria do not have to follow necessarily the same trend. Thus, if we compare all the chelates and mixtures of chelates tested, when working with EDDS and its mixtures the amount of iron in solution at the beginning of experiments is larger than that for the other mixtures, as has been reasoned in previous sections. Therefore, although there is competition between inactivation of bacteria and degradation of MPs, there is enough iron for contributing to both. However, in the case of EDTA and DTPA, these and their mixtures slowly release the iron and therefore there is less iron available in the reaction medium.

3.3. Phytotoxicity and BOD_5 assays

Biochemical oxygen Demand at 5 days ($mgO_2 L^{-1}$) is an important parameter in wastewater reuse for agricultural purposes. The Regulation of the European Parliament and of the Council (European Commission, 2020) lists the minimum requirements for agricultural wastewater reuse, establishing four water classes (A-D, A fixes $BOD_5 \leq 10$ $mgO_2 L^{-1}$ and B-D ≤ 25 $mgO_2 L^{-1}$). More information about the classes of reclaimed water quality can be found in Tables S2 and S3. In this study, BOD_5 at the end of the treatment was evaluated for all three organic fertilizers and their respective mixtures, when applied to MBR and CAS treatment (Fig. 6). In addition, phytotoxicity was evaluated

using seeds of *E. sativa*, with the aim of exploring if the final treated effluent could be used for agricultural purposes.

As can be observed in Fig. 6, using EDDS yielded the highest BOD_5 at the end of the treatment, for both matrices MBR and CAS. This behavior was expected because of EDDS was the more biodegradable chelating agent among those tested. The experiments conducted with mixtures containing EDDS also exhibited high values of BOD_5, especially in the case of MBR. However, in the case of CAS, experiments with only EDDS showed significantly high BOD_5 values, whereas the rest of chelators and respective mixtures show very similar values.

Finally, all treated MBR effluents were suitable for reuse for agricultural purposes, according to the values listed in the Regulation for agricultural water reuse (European Commission, 2020) (Tables S2 and S3). Nevertheless, taking into account the values of *E.coli* at the end of the treatment in CAS matrix, these effluents were not appropriate for this use, even though the BOD_5 values were within the range for their reuse.

Regarding phytotoxicity, Table 2 displays the germination index (GI) at different reaction times for MBR and CAS matrices. The equations for GI estimation can be found in Table S1. The control tests were carried out in deionized water.

Zucconi et al. (1981a, 1981b) proposed different categories depending on the percentage of GI to determine the phytotoxicity grade:

- Inhibition of seed germination and root elongation: <20% GI.
- Presence of phytotoxicity: 20–50% GI.
- No significant injury to the plant: >50–60% GI.
- Disappearance of phytotoxicity: >80–85% GI.
- Stimulation of the root elongation: >100% GI (better than control, which represent 100% of GI)).

As can be observed, at initial time only experiments with EDTA and DTPA showed a stimulation of the root in MBR. Nevertheless, the other experiments did not present phytotoxicity at initial time. On the contrary, in CAS matrix all treatments displayed values of GI > 100%, being this indicative of root stimulation. This difference between both matrices could be related to the higher organic matter content present in CAS compared to MBR, which can stimulate the growth of seeds. Regarding the differences between employed chelators, these could be associated to their effectiveness as fertilizers, being EDTA and DTPA those more employed in agriculture. The percentage of GI varied without a clear trend (between 15 min and 120 min), in all experiments. This fact was likely due to the presence of by-products (Freitas et al., 2017) probably more toxic than the initial MPs, as well as to transformation products from the chelating agents. However, evidences for phytotoxicity, inhibition of seed germination or root elongation were not observed.
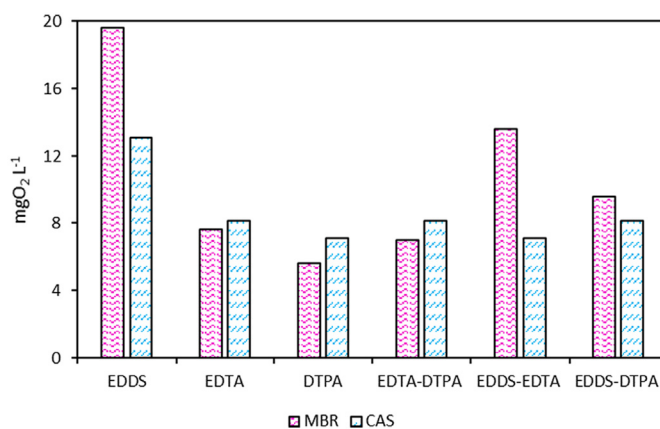

Fig. 6. Biochemical Oxygen Demand at 5 days at the end of the treatment with photo-Fenton at natural pH, using EDDS, EDTA, DTPA and three mixtures of these organic fertilizers, in MBR and CAS matrices. $[Fe]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}.

Table 2
Percentage of germination index of *E. sativa* in MBR and CAS matrix with photo-Fenton process at natural pH using DTPA, EDTA, EDDS and three different combinations of these chelating agents. $[Fe]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}.

Matrix	(%)	EDDS	EDTA	DTPA	50%EDDS 50%EDTA	50%EDDS 50%DTPA	50%EDTA 50%DTPA
MBR	0 min	76	153	117	68	96	86
	15 min	82	96	97	80	102	236
	30 min	108	71	132	63	119	202
	60 min	106	175	51	82	89	207
	120 min	79	139	73	67	132	209
	180 min	148	223	187	132	199	172
CAS	0 min	136	215	109	148	119	198
	15 min	51	93	150	104	112	93
	30 min	132	138	114	122	134	73
	60 min	126	154	101	104	193	185
	120 min	112	111	243	116	151	106
	180 min	168	186	122	237	151	139

Probably, the different changes in the experiments were caused by the distinct kinetics of MPs removal, implying different by-products formation and subsequent removal. In CAS, the tendency in all treatments to show lower values of GI throughout the experiment was minor than that in MBR. In that case, as the degradations of all three MPs were slower, the subsequent formation of more toxic by-products could also be minor causing the observed trend.

To conclude, at the end of the treatment, final treated effluents displayed values of GI higher than 100% (stimulation of the root) for both matrices MBR and CAS and for different chelating agents and their mixtures. This fact means that these effluents would be suitable for its reuse in agricultural irrigation without causing any damage to crops, as long as in CAS matrix the final values of *E.coli* are within the legal limit.

4. Conclusions

The capability of three Fe-complexes (EDDS, EDTA and DTPA) as iron sources has been demonstrated in photo-Fenton process for micropollutants abatement in Membrane Bioreactor and Conventional Activated Sludge effluents.

Propranolol and sulfamethoxazole have been successfully removed from MBR with three organic fertilizers achieving degradations higher than 70% at 180 min (2.31 kJ L^{-1}). Acetamiprid presented the lowest removals: 67.6% was the maximum degradation reached by EDTA at 180 min. This fact was related to the low kinetics of reactions between hydroxyl radical and this compound.

Regarding the differences between the two wastewaters tested, the MPs removals at the end of the treatment with CAS were always lower than those observed in MBR, due to the higher complexity of the matrix and its higher organic load. Additionally, the higher hardness of CAS promoted the higher precipitation of iron when treating this water, decreasing the efficiency of the process. For instance, when EDDS was employed, 90% of propranolol abatement was achieved at 30 min (0.39 kJ L^{-1}) with MBR while only 46.9% was reached with CAS at 180 min (2.31 kJ L^{-1}).

Concerning the Fe-complexes, the one with EDDS allowed the fastest degradation rate until the first 30 min, and then the reaction stopped failing to reach the complete degradation of the model micropollutants. For its part, the use of EDTA as chelating agent also yielded good kinetics, achieving the total degradation in propranolol and sulfamethoxazole. The lowest reaction rate was observed in experiments with DTPA. The different stability of organic fertilizers with iron affects degradation kinetics of MPs as well as iron release. To solve these inconveniences, three mixtures of organic fertilizers were also tested (50%EDDS +50%EDTA; 50%EDDS +50%DTPA; 50%EDTA +50%DTPA). In all three cases, a yield improvement was observed in experiments with both

MBR and CAS, compared to the treatment using the chelates separately. The mixture of EDDS + EDTA gave the best results reducing the treatment time about four and two times in propranolol removal compared to single EDDS and EDTA, respectively. Additionally, final soluble iron availability was 30% higher with the corresponding mixture, compared to the use of single EDDS. *E.coli* inactivation was also evaluated in CAS matrix, with EDDS + EDTA and EDDS + DTPA mixtures achieving the best inactivation at the end of the treatment with 2.1 log-inactivation.

Finally, the results obtained in BOD$_5$ tests and phytotoxicity suggested the suitability of both treated effluents MBR and CAS for its reuse in irrigation. Additionally, in CAS effluent the inactivation values of *E.coli* were within the legal limits for its application.

CRediT authorship contribution statement

N. López-Vinent: Conceptualization, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration. **A. Cruz-Alcalde:** Conceptualization, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration. **J. Giménez:** Writing – review & editing, Supervision, Project administration. **S. Esplugas:** Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.147416.

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