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Assessing the Synergies of Photo-Fenton at Natural pH and Granular Activated Carbon as a Quaternary Treatment

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Abstract: The challenge of microcontaminants (MCs) in wastewater effluent has been addressed by using different technologies, including advanced oxidation processes (AOPs) and adsorption. This work evaluates the benefits and synergies of combining these two processes. The AOPs were photo-Fenton and UV/H_2O_2 operated under natural pH but with different reagents dosages, lamps, and chelating agents. Chelating agents were used at analytical (ethylenediamine-N,N-disuccinic acid and citric acid) and technical grade (citric acid) to simulate scaling-up conditions. The adsorption process was studied via granular activated carbon (GAC) filtration using fresh and regenerated GAC. Four AOP scenarios were selected and coupled with GAC filtration, showing benefits for both processes. AOP treatment time decreased from 10–15 min to 5 min, resulting in a reduction in energy consumption of between 50 and 66%. In the photo-Fenton process, it was possible to work with low reagent dosages (1.5 mg L^{-1} iron and 20 mg L^{-1} of H_2O_2). However, the use of UV/H_2O_2 showed close removal, highlighting it as a real alternative. An extension of the GAC lifetime by up to 11 times was obtained in all the scenarios, being higher for regenerated than for fresh GAC. Furthermore, the toxicity and phytotoxicity of the treated wastewater were evaluated, and no acute toxicity or slight variation in the phytotoxicity was observed in the combination of these processes.

Keywords: contaminants of emerging concern; micropollutant; process combination; real wastewater; water remediation

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1. Introduction

The growing presence of microcontaminants (MCs) in surface water poses a challenge to their mitigation, identifying the point source, and implementing technical solutions as for the wastewater treatment plants (WWTPs) [1]. MCs are organic molecules, such as personal care products, pharmaceuticals, pesticides, and herbicides, that are highly recalcitrant and are only partially removed in conventional WWTPs [2]. Despite their low concentration (µg or ng L^{-1}), they can potentially affect water bodies due to their risk to aquatic life and human health [3,4].

In response to this concern, the European Union (EU) has developed a new proposal for a Directive of the European Parliament and of the Council concerning urban wastewater treatment (UWWTD) [5]. The new recast of the exiting UWWTD tackles the MCs problem for the first time, alongside more restrictive limits for nitrogen and phosphorous emissions, including the necessity to achieve energy neutrality in WWTPs. Regarding MCs, quaternary treatments should be installed in WWTPs treating a load of 150,000 p.e. and above to reduce the MC emissions and preserve the quality of receiving water bodies. However, the necessity of installing quaternary treatments in rural areas (up to 10,000 p.e.) is also proposed in urban WWTPs that represent a risk to human health or the environment. The required removal was defined as a minimum of 80% of 12 MCs, which were selected as the most representative, that should be measured in the dry season when a higher MC concentration is expected. The new proposal defines WWTPs as relevant actors in the

European Green Deal; consequently, it marks the necessity of achieving energy neutrality by 2045. Therefore, quaternary treatment should not increase the consumption of energy significantly.

Previously to the recast of the existing UWWTD, several countries, such as Luxembourg and Switzerland, adopted precautionary measures and regulated the removal of MCs from wastewater [6,7]. Luxembourg proposed the 80% removal of four mandatory MCs—diclofenac, carbamazepine, clarithromycin, and benzotriazole—from the inlet to the outlet of WWTPs, selected due to their relevance for local water bodies. This choice anticipated the EU strategy, as the four MCs are included in the 12 selected MCs from the new directive. The Luxembourgish regulation is expected to be adapted to new EU requirements in the coming years.

Several technologies have been studied as candidates for quaternary treatment for the removal of MCs. Despite efficient removal, they showed significant drawbacks, such as the generation of toxic by-products, the production of high-concentration brines, high space requirements [8,9], etc. In order to address this issue in a real scenario, some works have recognised the coupling of technologies of different natures as a suitable solution [10].

Advanced oxidation processes (AOPs) are very interesting technologies, as they mineralise the MCs instead of separating them from one phase to another or concentrating them as the membranes do. They are based on the production of hydroxyl radicals ($^\bullet$OH) [11], which react non-selectively with the pollutants and are very powerful for MC degradation. AOPs are highly efficient in producing $^\bullet$OH and do not generate bromates and carbonyl-related side products, in contrast to ozonation. One of the most studied AOP relies on UV/H_2O_2, which is based on the absorption of UV-C light (254 nm) by hydrogen peroxide (H_2O_2), which then generates $^\bullet$OH [12]. The photo-Fenton process poses a very promising alternative to conventional AOPs due to its higher capacity to remove MCs, which is, in theory, even higher than the UV/H_2O_2 process [13]. The photo-Fenton process is based on the Fenton reaction in which iron and H_2O_2 are in contact, producing $^\bullet$OH. In the photo-Fenton process, UV radiation is applied to regenerate iron (III) to iron (II) and increment $^\bullet$OH production [14]. The pH strongly affects the efficiency of the process, with the optimal pH being 2.8.; working at natural pH is not possible, as the iron is known to precipitate. Operating at acidic pH in a WWTP is not feasible due to the complexity associated with the acidification and neutralisation steps required. Thus, chelating agents are presented as the key to keeping the iron in solution at natural pH. The chelating agents are organic molecules, such as ethylenediamine-N,N-disuccinic acid (EDDS), nitrilotriacetic acid (NTA), oxalic acid, or citric acid, that can form bonds with iron and avoid its precipitation. The stability and efficiency of the chelating agents at neutral pH allow for the removal of up to 80% of carbamazepine when working with NTA [15] or EDDS [16]. Moreover, the coupling of the photo-Fenton process at neutral pH with adsorption to remove MCs has rarely been performed [17,18]. To the best of our knowledge, all the works analysing MCs removal were carried out under solar irradiance (solar photo-Fenton). Still, this condition limits the application of the photo-Fenton process to sunny hours; thus, water can only be treated for a few hours per day. This means that the technology is not feasible in a WWTP that receives water all day long or in areas with low solar irradiation. Considering these climatic conditions, medium-pressure (MP) UV lamps (instead of sunlight) were used as a light source.

Adsorption processes are consolidated technologies that transfer MCs from the water matrix to an adsorbent material. Granular activated carbon (GAC) filtration is a robust technology that is easy to implement and operate. The capacity to remove MCs has been widely demonstrated, up to 80% of carbamazepine or diclofenac can be adsorbed in GAC filtration [19]. The removal percentage by GAC filtration lies in the affinity of the MC with the selected GAC [19,20]. The main drawback is the necessity to replace it once the exhaustion is achieved. In recent years, regenerated GAC has been shown to be an alternative to reduce waste, energy consumption, and carbon footprint [13,21]. Thus, in this study, a comparison between commercial fresh and regenerated GAC is also performed.

The GAC filtration test needs a long operation time of several months to reach the breakthrough and achieve exhaustion. In order to address this problem, Crittenden et al. [22] proposed the use of a rapid small-scale column test (RSSCT) as a bench-scale alternative that can reach the breakthrough in days, reducing the operation time and the amount of water required for the experiments. The results obtained using the RSSCT are not directly comparable to the full-scale treatment results, but they allow for a comparison between the performance of different GACs [23]. Despite its limitations, this test is the preferred process when selecting the best GAC and indicatively predicting pollution behaviour in GAC columns.

This work studied the coupling of two processes: AOPs and GAC filtration. Despite previous research on the coupling of the photo-Fenton process and adsorption tested it with dyes [18], has been rarely proposed to remove MCs with photo-Fenton at natural pH [17]. Specifically, to the best of our knowledge, this work studies the coupling of both technologies to remove MCs at natural pH, using lamps as a source of irradiation for the very first time. The use of the solar photo-Fenton process has been deeply evaluated, but the use of lamps is mostly studied at the lab scale [24–26], in contrast to the pilot scale of this study. Furthermore, operating at natural pH (7–7.5) was a requirement to avoid initial acidification, later neutralisation, and a consequent increase in effluent salinity. In addition, RSSCTs were performed as stand-alone and coupled systems, which allowed for a comparison of GAC lifetime, in contrast to the general approach of performing batch tests that are far from representing the real operation.

The main target and novelty of this work is the focus on exploring the synergies and benefits of the combination, unlike other studies that combine different technologies to improve removal efficiency [27–29]. The potential benefits are mainly associated with cost reduction, GAC lifetime extension, exploring the possibilities of using regenerated GAC (lowering carbon footprint), a reduction in the reagents in the AOPs, or a reduction in treatment time, thus reducing energy consumption and coming closer to energy neutrality. The possible synergies are related to the most recalcitrant MC, which are different for each technology. The first step was the AOP, which was applied as a polishing step to reduce the MCs' concentration but not completely eliminate them. Thus, it can be operated with lower reagent doses and treatment times. This approach will advance the scaling up of the photo-Fenton process. Additionally, technical-grade reagents at natural pH and lamps for UV irradiation were used to study the most realistic scenario in Luxembourg.

Therefore, the main objective of the present work was to reach 80% removal of benzotriazole, carbamazepine, clarithromycin, and diclofenac via (1) photo-Fenton, (2) UV/H_2O_2, (3) GAC filtration, and (4) the coupling of GAC with the two previous AOPs. Different photo-Fenton scenarios were tested for the best operational conditions, modifying diverse parameters, e.g., type of lamps, reagent dosage, or pH. Additionally, the feasibility of the regenerated GAC was compared to fresh. The best scenarios from AOPs were performed on the coupling of technologies. Toxicity was analysed (as acute toxicity and phototoxicity) to assess the suitability of the technologies and select the best technology not only in terms of MCs removal but also in considering the quality of the influent of the treatments.

2. Materials and Methods

2.1. Chemicals

Benzotriazole, carbamazepine, clarithromycin, and diclofenac (purity ≥99% HPLC Standards GmbH, Borsdorf, Germany) were spiked in the water matrix to increase the concentration to 1 $\mu g\ L^{-1}$ for benzotriazole and diclofenac and 2 $\mu g\ L^{-1}$ for carbamazepine and clarithromycin. Two sources of iron were used: ferric sulphate heptahydrate (97%, Sigma-Aldrich, Hamburg, Geramany (analytic grade)) and iron sulphate solution (12%, Dr Paul Lohman GmbH, Emmerthal, Germanu (technical grade)). The iron was initially chelated with EDDS (35%, Sigma Aldrich) and subsequently with analytic citric acid (99%, CarlRoth GmbH., Karlsruhe, Germany) and technical citric acid (StockMeier Chemie Dillenburg GmbH., Dillenburg, Germany). Ammonium acetate (98%), ortho-phenanthroline (99%), ascorbic acid (99%), and sodium thiosulfate (98%) from Sigma-Aldrich were used to measure iron and H_2O_2 concentration. Bovine catalase (Sigma-Aldirch, Hamburg, Germany) was added to all the samples to consume the H_2O_2 and quench the Fenton reaction.

2.2. Water Matrix

MC removal was tested in municipal wastewater effluent from the Heiderscheidergrund municipal WWTP (12,000 p.e., Luxembourg), which was collected after the clarifier and thus treated with a conventional activated sludge process. The main characteristics of the wastewater were the following: pH: 6.9–7.7, 400–640 µS cm^{-1} of conductivity, 80–150 mg HCO_3 L^{-1}, 9.7–18 mg L^{-1} of chemical oxygen demand (COD), 1.1–5 mg L^{-1} of total nitrogen (TN), 0.66–2.5 mg L^{-1} of NH_4^+–N, 0.23–2.2 mg L^{-1} of NO_3^-–N, and 0.85–3.3 mg L^{-1} of total phosphorus (yearly range, 2022).

2.3. Analytical Determination

Benzotriazole, carbamazepine, clarithromycin, and diclofenac were analysed externally (Luxembourg Institute of Science and Technology LIST, Luxembourg). The samples were pre-concentrated before the injection by solid phase extraction. Then, they were injected in liquid chromatography (Agilent 1200 SL LC) coupled in tandem with mass spectrometry (LC-MS/MS), a Hybrid Quadrupole-Linear Ion Trap instrument (Sciex 4500 QTrap) with electrospray ionisation in positive polarity. Venditti et al. [30] previously described the methodology; the recovery rates, relative standard deviations, and limits of quantification (LoQ) of MCs are defined in Table S1 of the supplementary information. The H_2O_2 concentration was monitored using the spectrophotometric method with titanium oxysulfate (DIN 38402 H15). The total and dissolved iron were determined via the ortho-phenanthroline method at 510 nm (ISO 6332 [31]). A UV6300 PC Double Beam spectrophotometer from VWR was used for both analyses.

A pH/conductometer 3320 from WTW was used to monitor pH and conductivity. Hach-Langue kits measured COD (LCK 1414), TN (LCK 238), NH_4^+–N (LCK 304), NO_3^-–N (LCK 339), and total phosphorus (LCK 349).

2.4. Experimental Setup

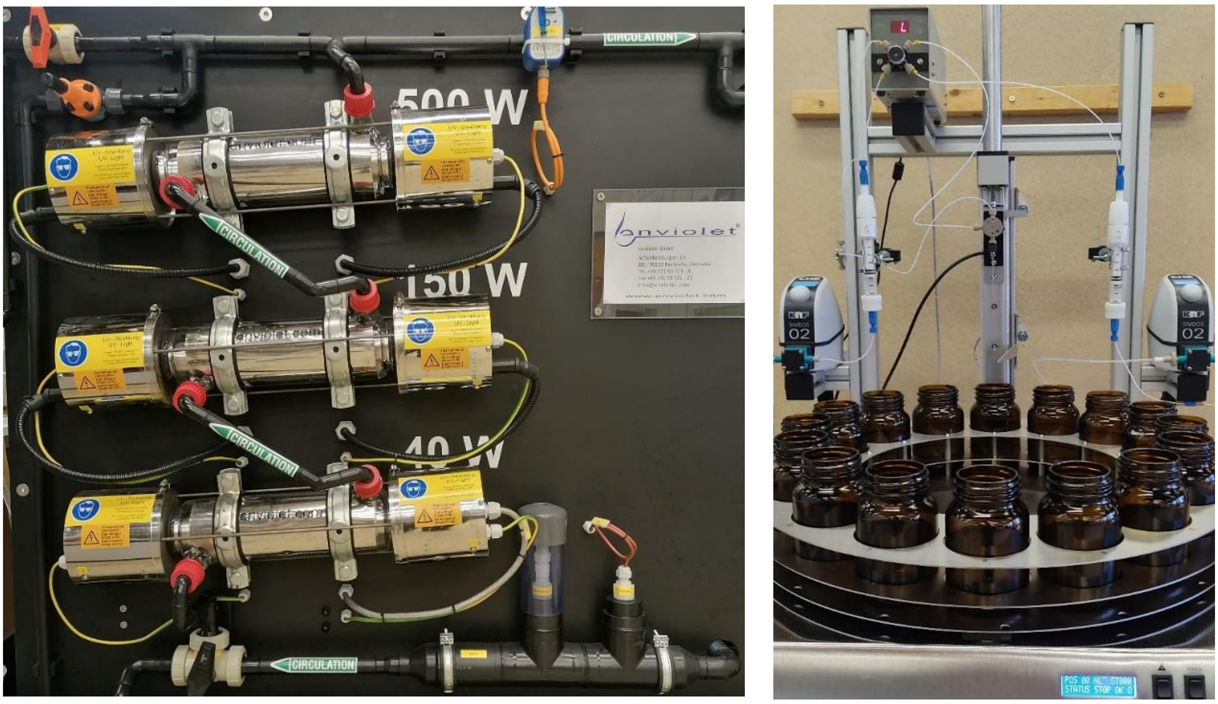
2.4.1. Photo-Fenton Systems

The photo-Fenton system, previously described by Núnez-Tafalla et al. [18], consisted of three borosilicate reactors in series connected to a tank and working in batch mode (Figure 1a). The flow was 800 L h^{-1}, provided by a centrifugal pump (Schmitt MPN115 (0.25 kW)); this flow ensured a turbulent regime. Each reactor contained a different lamp: a 500 W MP lamp (89 W in UV), a 150 W MP lamp (45 W in UV), and a 40 W low-pressure (LP) lamp (11 W in UV). The MP lamp provided polychromatic irradiation compared to the LP lamp, with two irradiation peaks at 185 and 254 nm. The system allowed for all the lamps to be simultaneously or separately switched on. The reactor's external surface was 0.1 cm^2, and the volume was 1.2 L, meaning a hydraulic retention time (or irradiation time) of 5.5 s. During the process, the temperature was controlled and maintained between 18 and 25 °C to avoid lamp damage.

The tank was filled with 60 L of the water and spiked with benzotriazole, carbamazepine, clarithromycin, and diclofenac (the concentration range was 1.5–1.9, 3.3–4.8, 1.3–2.8, and 1.1–2.5 µg L^{-1}, respectively) and then homogenised by recirculating the solution for 15 min. Then, the preprepared iron complex was added and recirculated for 15 min. Finally, H_2O_2 was added, and the moment the lamps were switched on was considered time zero. The iron complex was prepared by dissolving iron sulphate in acidic water. Once it was totally dissolved, the chelating agent was added and stirred until complete complex formation. The molar ratio concentration was 1:1 for both chelating agents, EDDS, and citric acid, as shown by other authors as the most suitable value [32]. The samples were taken at predetermined times, and the bovine catalase solution (0.1 g L^{-1}) was added to the samples to remove the residual H_2O_2 and stop the Fenton reaction. The results were graphically represented by setting the operating time in minutes on the abscissa axis and the normalised effluent concentration (C/C0) on the ordinate axis, which is calculated as shown in Equation (1):

$$\mathit{Normalised\ concentration} = \mathrm{C}/\mathrm{C}_0 = \frac{\mathrm{C}_i}{\mathrm{C}_0} \tag{1}$$

where C is the concentration in the water matrix at time i, and C_0 is the initial concentration.



(**a**) (**b**)

Figure 1. (**a**) Photo-Fenton equipment; (**b**) RSSC equipment.

2.4.2. Rapid Small-Scale Columns

The RSSC (Figure 1b) system was designed based on the study by Zietzschmann et al. [33]. It consisted of two glass columns operated in parallel, with a diameter of 8 mm and a length of 100 mm; the empty bed volume was adjustable. The water, spiked with the desired MCs concentration, was stirred until complete homogenisation and was stored in a 50 L tank from which the columns were fed simultaneously by a diaphragm pump (KNF Simdos 02, KNF DAC GmbH). An autosampler (AutoSam 2.3, Hitec Zang) allowed for samples to be taken at preprogrammed times. The operational conditions were stabilised in 1 mL of empty bed volume and a flow of 10 mL min^{-1}. A sample was taken from the tank and was considered the initial concentration.

Two commercial GACs were studied within the project: a fresh GAC CarboTech DGF 8 × 30 GL (Carbo Tech Ac Gmbh. Essen, Germany) and a regenerated one, CarboTech Pool W1-3 (CarboTech Ac Gmbh, Essen, Germany) (being CarboTech DGF 8 × 30 GL after reconditioning). Table S2 shows their main physicochemical properties. The GAC was preprocessed to avoid wall effects on the columns. It was crushed with a mortar and pestle, sieved to obtain a uniform size of between 100 and 500 µm, rinsed with deionised water, and dried in the oven. The GAC was brought in the columns, using glass wool as a retainer.

The breakthrough of the adsorption process on the columns was graphically represented, setting the abscissa axis as the bed volumes (BV) and normalised effluent concentration (C/C_0, C and C_0 are the outlet and inlet concentrations, respectively) as the ordinate axis. BV is a dimensionless parameter that describes the relationship between the volume feed and the volume of the column at a defined operation time. The breakthrough was considered to be the time between C/C_0 equal to 0.05 and 0.95 [34]. The breakthrough was modelled and fit according to the hypothesis that the adsorption of the MCs follows a first-order kinetic model, as described in Equation (2) [18]:

$$\frac{C}{C_0} = \frac{qKBV}{1 + KBV} \tag{2}$$

where C is the concentration at time t, C_0 is the initial concentration, q and K are adsorption parameters, and BV is the BV at which the effluent concentration is measured.

When working with an adsorption system, 80% MC removal corresponds to C/C_0 = 0.20 (meaning a maximum of 20% of MCs released into the environment), which is defined as 20 BT. The order in which the MCs achieved 20 BT can be used to scale up the process and predict the time of GAC replace. On the contrary, the BV in which 20 BT was achieved in the RSSCT could not directly correlate with a full-scale installation due to various influencing factors, such as the fouling produced by the organic matter [23].

2.4.3. Coupling of Advance Oxidation Processes and Granular Activated Carbon

AOP was selected as the first step when coupling technologies. Four scenarios of AOP were operated and evaluated, varying the selected process (photo-Fenton or UV/H_2O_2) and the chelating agents: EDDS, analytic citric acid, and technical citric acid. The final selection was based on the best performance and also an assessment of practical feasibility at full scale. The AOP was run for 5 min (5.5 s of irradiation time), then the lamps were switched off. Bovine catalase was added to the tank to remove the residual H_2O_2 and stop the Fenton reaction. The AOP effluent was transferred to the RSSCT feeding tank, and the MC adsorption was evaluated under the same conditions as the stand-alone process for both GAC types. In order to determine the possible extension of GAC lifetime, C0 was the concentration of the untreated water before the photo-Fenton process.

2.5. Experimental Design

The tests of this study were performed in five phases:

Phase 1: Assess the best lamp type (monochromatic versus polychromatic irradiation, LP and MP, respectively) to maximise MC removal in the lowest process time (UV/H_2O_2 and photo-Fenton).

Phase 2: Assess the best iron and H_2O_2 dosage, prioritising the minimisation of iron and aiming at the lowest reagent concentration possible, irradiation with the best lamp from Phase 1, and using EDDS as a chelating agent (analytical grade).

Phase 3: Assess the suitability of the best dosage from Phase 1 with citric acid as a technical-grade, commercially available chelating agent.

Phase 4: Removal of the iron (no iron) dosage and assess the best H_2O_2 concentration.

Phase 5: Perform a comparative characterisation of fresh and regenerated GAC (stand-alone).

Phase 6: Use a combination of the technologies, applying the best scenarios of the AOP obtained in the previous phases (Phase 1 to 3) with the referred GACs (Phase 4) to find the best combination process conditions that maximise GAC lifetime within the same process time.

The best scenario was selected based on a removal (%) value obtained by calculating the average of the individual removals for the four mandatory MCs, as defined in the recast of the existing UWWTD [5].

2.6. Toxicity Test

Toxicity and phytotoxicity were analysed in the treated water for the AOPs and the coupling of technologies. For the AOPs, two samples were analysed: untreated water and the sample in which 80% removal was achieved. When the coupling of technologies was performed, four samples were tested: untreated water, water after 5 min of AOP treatment, and 4000 BV for fresh and regenerated GAC.

Acute toxicity was determined by *Daphnia Magna* immobilisation using a DAPHTOXKIT F kit (MicroBioTest Inc. (Gent, Belgium)). The lethal concentration, 50% (LC50), was evaluated at 24 and 48 h in a dilution row of 100% and 50%. Phytotoxicity was assessed in three species, *Lepidium sativum*, *Sinapis alba*, and *Sorghum saccharatum*, with the PHYTOTOXKIT for Liquid Samples kit (MicroBioTest Inc.). Seed germination and the root and leaf growth were analysed, showing the water matrix's germination rates, as well as the stimulation or inhibition effects on the roots and leaves.

3. Results and Discussion

3.1. AOP Experiments

The UV/H_2O_2 process using LP lamps and an initial H_2O_2 concentration of 40 mg L^{-1} was tested according to previous studies [18]. Figure S1 shows the removal of the average of the 4 MCs. A total of 80% removal of the average was achieved in 60 min. When looking at the performance of individual compounds, diclofenac appeared to be the first removed, which was expected due to its photosensitivity [35], while clarithromycin was the last. this behaviour was observed in all the AOP processes (Table S3). Therefore, clarithromycin was adopted as a control compound since it is the most recalcitrant. In the next experiments, iron was added to speed up the treatment process, resulting in a halved treatment time regarding UV/H_2O_2.

In the photo-Fenton test (with LP lamp), EDDS was chosen as the chelating agent due to its reported stability [36], with an iron concentration of 3 mg L^{-1} (molar ratio with EDDS 1:1). The first tests were performed upon using analytic iron and chelating agents. The average removal of MCs slightly increased, with less positive results than those previously reported [37,38]. This slight improvement allowed us to achieve the objective of removing 80% of the average of the compounds in 30 min. However, 80% clarithromycin removal was achieved in 60 min. The operational duration (minimum 30 min, meaning 33 s or irradiation time) was found to be too long for future full-scale implementation [39]. Therefore, the simultaneous operation of both LP and MP lamps was proposed to enhance the irradiation.

In the following test, the 500 W MP and 40 W LP lamps were used simultaneously with the previous reagent dosage: 3 mg L^{-1} of iron and 40 mg L^{-1} of H_2O_2. The average MC removal reached 60% in 5 min, and the objective was obtained in 10 min (Figure S2). However, 80% clarithromycin removal was achieved in 15 min. Looking at these results the iron dosage was reduced to 1.5 mg L^{-1} in order to mitigate iron release into the environment. The adjustments would align with recommendations in certain German regions, where the concentration limit in surface water bodies ranges between 0.7 and 1.8 mg L^{-1} [40]. The obtained removal rate was similar to the previous dosage, with 80% removal of the MC average in 10 min. The high difference in the treatment time between the 40 W LP lamp and its simultaneous use with the 500 W MP lamp suggested that the 500 W MP lamp was the main contributor; thus, the next tests used this lamp alone, and this reduced the energy applied for the treatment.

According to a previous study with the 500 W MP lamp [41], 5 mg L^{-1} of iron and 40 mg L^{-1} of H_2O_2 were tested, as well as 3 mg L^{-1} of iron and 40 mg L^{-1} of H_2O_2. In Figure 2, the removal of the average of the four compounds is shown to achieve 80% in both cases after 10 min (11 s of irradiance) of the process. In contrast, the results for clarithromycin removal were different, with the process taking 5 min less when 3 mg L^{-1} was dosed. These results could be related to the EDDS increment needed for a higher iron dosage, which raised the organic content of the solution consuming $^{\bullet}OH$ [42].

Once again, iron was reduced to 1.5 mg L^{-1}, and H_2O_2 was maintained at 40 mg L^{-1}. The MC removal rate was lower but close to previous tests, with 75% removal of the average in 10 min, reaching 80% after 15 min (16.5 s of irradiation time); clarithromycin was eliminated after 30 min. Lastly, H_2O_2 was reduced to 20 mg L^{-1}, showing a similar trend of 40 mg L^{-1}. The obtained results confirmed the possibility of working with a low reagent dosage. The effect was more remarkable for iron than for H_2O_2, which was reduced by up to 70%, considering previous works [25,43,44]. Reducing the iron concentration is also crucial for achieving the legal limits in water bodies. Furthermore, the treatment time was also much lower compared with previous work, as it decreased from 10 [45], 30 [25], or 180 min [46] to 16.5 s, which would reduce future costs remarkably on a larger scale.

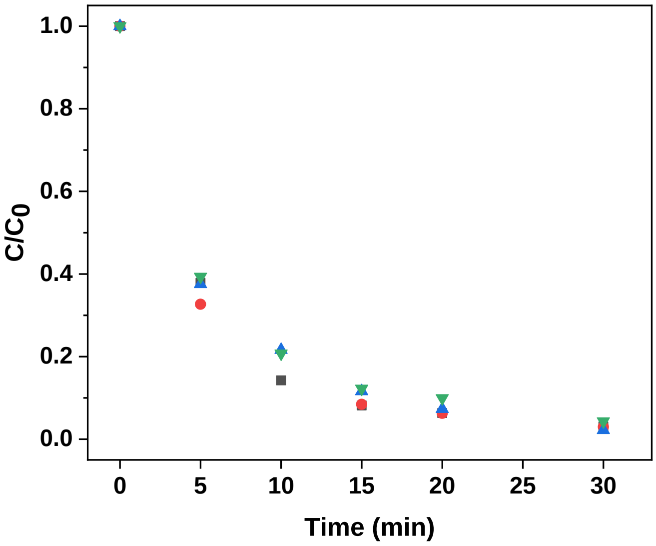


Figure 2. Average removal of four mandatory MCs using the photo-Fenton process, a 500 W MP lamp, and EDDS as a chelating agent. ■: 5 mg L^{-1} iron and 40 mg L^{-1} of H_2O_2; ●: 3 mg L^{-1} iron and 40 mg L^{-1} of H_2O_2; ▲: 1.5 mg L^{-1} iron and 40 mg L^{-1} of H_2O_2; ▼: 1.5 mg L^{-1} iron and 20 mg L^{-1} of H_2O_2.

As the combined photo-Fenton process aimed to reduce the MC concentration but not mineralize them, the removal of MCs after 5 min was compared (Figure 2), obtaining similar trend results under all conditions. Thus, 1.5 m L^{-1} of iron and 20 mg L^{-1} of H_2O_2 were selected for the following tests.

When anticipating the scaling up of the process in the future, alternative chelating agents available as industrial products were proposed since EDDS is highly expensive and difficult to find provided in large quantities from the market. Citric acid is a compound that is widely used in industry, is easy to handle (in the form of powder) at an affordable cost and is not toxic. Given its demonstrated suitability by previous authors [47], it was selected as the preferred option for potential future scale-up. Citric acid was used as an iron chelating agent for two iron forms: (i) analytical iron chelated with analytical-grade citric acid and (ii) technical-grade iron using technical-grade citric acid as chelating agents to properly assess the influence of the quality of the reagents in the performance of the process. A total of 80% average MCs removal was achieved with both iron:citric acid qualities in 15 min; a slight removal rate of the analytical iron:citric acid was observed, increasing the process time from 20 to 30 min for clarithromycin degradation. The slower removal when using citric acid as a chelating agent is related to the lower stability of the complex [48]. In contrast, the good performance of the technical-grade product was satisfactory, as previous works did not show the possibility of completely removing all the MCs [17,45]. This difference can be caused by the higher energy irradiated on the system, as previous works were performed under solar light. Figure 3 compares MC degradation with the three chelated iron sources (analytical-grade iron:EDDS, analytical iron:citric acid, and technical-grade iron:citric acid). These three scenarios were further studied on the coupled treatment.

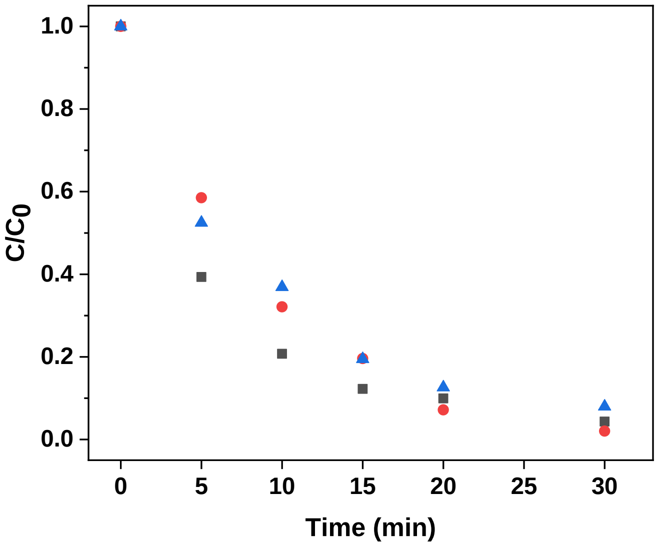


Figure 3. Average removal of four mandatory MCs using the photo-Fenton process, a 500 W MP lamp, 1.5 mg L^{-1} iron, and 20 mg L^{-1} of H_2O_2. ■: EDDS; ●: analytic citic acid; ▲: technical-grade citric acid.

UV/H_2O_2 (no iron) was also investigated using the 500 W MP lamp. Figure 4 shows the removal trend using 40 mg L^{-1}. A sharp removal was observed in the first minutes, achieving 80% of the MCs average removal in 10 min (11 s of irradiation time). As in the previous tests, diclofenac was the first to be removed (in 5 min), and clarithromycin was the most recalcitrant, needing 15 min to accomplish the objective (Table S3). The H_2O_2 dose was increased to 100 mg L^{-1}, with the aim of achieving higher degradation rates. The results were similar to the previous test; the close results can be related to an excess of H_2O_2 that quenches $^{\bullet}$OH by producing hydroperoxyl radicals [49], which has been previously reported by other authors [7]. Considering this phenomenon, the H_2O_2 dosage was reduced to 20 mg L^{-1} of H_2O_2. Under this condition, removal rates were slower, reaching 80% average removal in 15 min and for clarithromycin in 20 min. Therefore, UV/H_2O_2 with 40 mg L^{-1} was selected to be coupled with GAC filtration. Table 1 presents a comprehensive summary of the key parameters from the tests, providing clear evidence to support and validate the selected scenario.

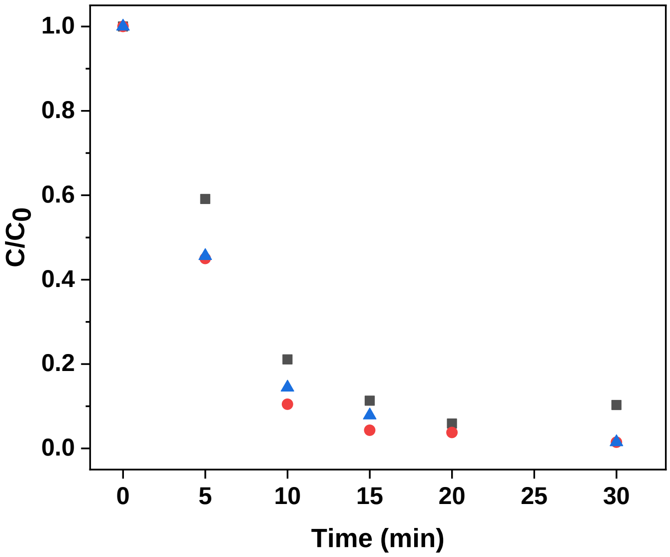


Figure 4. Average removal of four mandatory MCs using the UV/H_2O_2 process and a 500 W MP lamp. ■: 20 mg L^{-1} of H_2O_2; ●: 40 mg L^{-1}; ▲: 100 mg L^{-1}.

Table 1. Time, energy consumption, H_2O_2 consumption, and dissolved iron concentration at the point when 80% removal of the average four mandatory MCs was achieved during the AOP tests.

	Time (min)	Energy (kWh)	H_2O_2 (mg L^{-1})	Diss. Iron (mg L^{-1})
UV/H_2O_2: 40 W LP lamp 40 mg L^{-1} of H_2O_2	60	40	5.1	--
Photo-Fenton: 40 W LP lamp 3 mg L^{-1} of iron and 40 mg L^{-1} of H_2O_2	60	40	14.2	2.6
Photo-Fenton: 500 W + 40 W 3 mg L^{-1} of iron 40 mg L^{-1} of H_2O_2	10	90	8.8	3.0
Photo-Fenton: 500 W + 40 W 1.5 mg L^{-1} of iron 40 mg L^{-1} of H_2O_2	10	90	4.8	1.6
Photo-Fenton: Fe:EDDS 5 mg $L^{-1,}$ of iron 40 mg L^{-1} of H_2O_2	10	83	9.2	4.7
Photo-Fenton: Fe:EDDS 3 mg L^{-1} of iron 40 mg L^{-1} of H_2O_2	10	83	6.2	3.0
Photo-Fenton: Fe:EDDS 1.5 mg L^{-1} of iron 40 mg L^{-1} of H_2O_2	15	125	5.0	1.4
Photo-Fenton: Fe:EDDS 1.5 mg L^{-1} of iron 20 mg L^{-1} of H_2O_2	15	125	5.2	1.5
Photo-Fenton: Fe:Citric Acid Analytical-grade 1.5 mg L^{-1} of iron 20 mg L^{-1} of H_2O_2	15	125	3.9	1.5
Photo-Fenton: Fe:Citric Acid Technical-grade 1.5 mg L^{-1} of iron 20 mg L^{-1} of H_2O_2	15	125	3.8	1.7
UV/H_2O_2: 500 W 20 mg L^{-1} of H_2O_2	15	125	3.0	--
UV/H_2O_2: 500 W 40 mg L^{-1} of H_2O_2	10	83	5.0	--
UV/H_2O_2: 500 W 100 mg L^{-1} of H_2O_2	10	83	6.7	--

3.2. Adsorption Process

The adsorption capacity depends on a wide range of compound characteristics, such as the polarity or the molecular weight. A determinant characteristic for the adsorption of MCs is their hydrophobic nature, which is usually described by the octanol-water partition coefficient (K_{OW}) represented by the log K_{OW}. The affinity of each pollutant to adsorption can thus be categorised as follows: low adsorption affinity (log $K_{OW} < 2.5$), medium adsorption affinity ($2.5 <$ log $K_{OW} < 4$), and high adsorption affinity (log $K_{OW} > 4$) [50]. The K_{OW} values of the target compounds are shown in Table S4. The water matrix content has also been described as a determinant of the adsorption of MCs, as dissolved organic matter competes with MCs for the adsorption sites [51].

Figure 5 shows the breakthrough of the average of the MCs adsorption for the fresh and the regenerated GAC. The breakthrough was fitted following the model described in Equation (2); the values of the model are shown in Table S5. The model was used to calculate the adsorption capacity for both GACs. The results were similar since the regenerated GAC was produced from the fresh GAC, attaining the average MCs 20 BT in 1080 and 720 BV for fresh and regenerated GAC, respectively. Diclofenac was the first to achieve 20 BT at 400 BV for both GAC types. Diclofenac is a strong competitor for the adsorption sites, quickly occupying the available adsorption sites [2], thus, it has been reported as one of the first compounds to show signs of a breakthrough (Table S6). The second MC to achieve 20 BT was clarithromycin, showing a higher difference between adsorbent materials, reaching 20 BT in 1000 BV and 500 BV for fresh and regenerated GAC, respectively. Next, carbamazepine and benzotriazole achieved the breakthroughs (third and fourth, respectively). The order of reaching 20 BT was directly related to the molecular mass (Table S4). The similar performance of both materials evidenced the possibility of implementing regenerated GAC at full scale, lowering the carbon footprint.

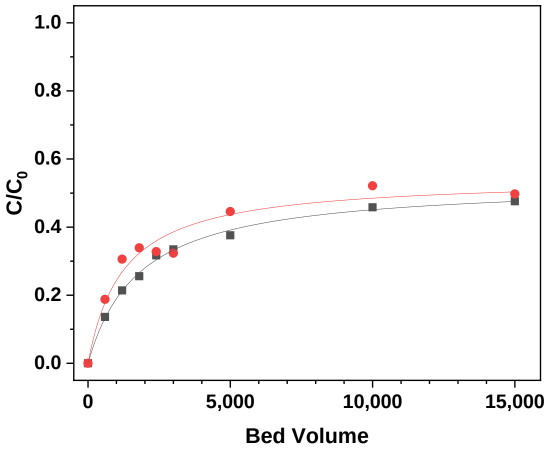


Figure 5. MC average breakthrough of ■ CarboTech DGF 8 × 30 GL (fresh GAC) and ● CarboTech Pool W1-3 (regenerated GAC).

3.3. AOP and Adsorption Process Combination

Four scenarios were selected to study the benefits of the coupling of these technologies. The scenarios were selected to analyse from the most favourable scenarios at the lab scale (EDDS) to the most realistic setup for a future scale-up, such as technical-grade iron and citric acid. All cases showed a GAC lifetime extension for diclofenac, which was the first to achieve 20 BT in the GAC stand-alone filtration and was quickly removed by AOPs. However, the influence on GAC lifetime should be considered due to the presence of technical-grade product excipients, which can block the pores of the GAC.

Figure 6 shows the percentage of removal attained by each process within the 80% target for the average of the MCs in the different scenarios. The BV when 80% was achieved is shown above the bars. The first bar shows the GAC stand-alone, which was used to facilitate a comparison of the extension of the GAC lifetime.

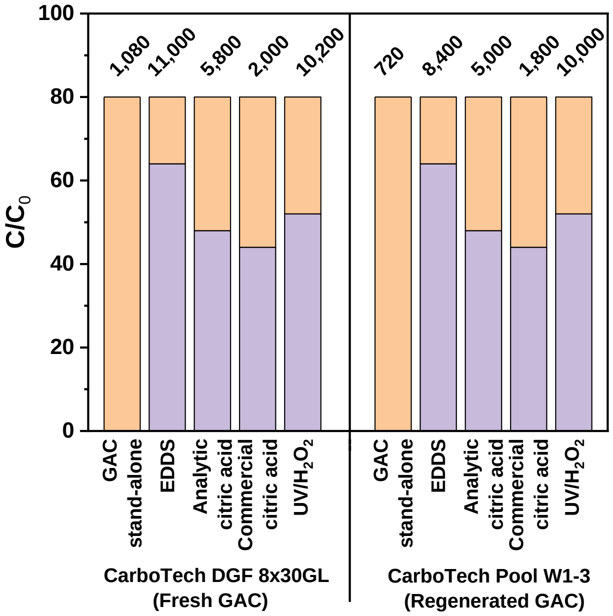


Figure 6. Contribution of each step of the coupled treatment (until 80% target) in the four selected scenarios (orange: removal by adsorption; purple: removal by the AOP). The bed volumes when 80% removal was achieved can be seen above the bars.

When using iron: EDDS, 1.5 mg L^{-1} of iron and 20 mg L^{-1} of H_2O_2, 64% of the average MC was removed in the photo-Fenton treatment, eliminating up to 72% of diclofenac. Thanks to the high removal of diclofenac, the fresh and regenerated GAC lifetime was extended up to 10 and 11 times, respectively. When the MCs were analysed separately, the first to achieve the minimum removal limit was clarithromycin, and the second was diclofenac. Up to 80% of the benzotriazole was removed in all the tests.

The removal in the first step, AOP, was close to those observed by previous authors [27,29]. Still, in the present work, iron concentration was reduced from 5 mg L^{-1} to 1.5 mg L^{-1}, and H_2O_2 was reduced from concentrations between 50 and 150 mg L^{-1} to 20 mg L^{-1}. Moreover, the treatment time was reduced since solar irradiation has a lower irradiance than lamps. These results highlight the benefits of working with UV lamps instead of solar irradiation. From the previous investigations, it is highlighted that even when working at acidic pH and high reagent dosage, it is necessary to evaluate the toxicity of the matrix, as several by-products are generated and not removed in the adsorption step. The GAC phase in the previous works was, in general, performed in batch mode, so no comparison was possible.

When using citric acid as a chelating agent, the efficiency of the photo-Fenton process was reduced, as observed in the previous test, with 48% and 44% removal for analytical- and technical-grade chemicals. The GAC lifetime was extended 5 and 7 times for fresh and regenerated GAC, respectively, when analytic iron and citric acid were used in the AOP. When the technical grade chemicals were employed, this extension was reduced to 2 and 2.5 for fresh and regenerated GAC. The difference between analytical-grade and technical-grade products highlights the necessity of testing products similar to those on a large scale. The lower extension of the GAC lifetime when technical-grade chemicals were used could not be exclusively related to the lower removal in the first step, as it was close to the analytical grade. This effect can be caused by competition for the adsorption sites with the excipients contained in the technical reagents.; the iron source contained only 12% iron, meaning 88% constituted other additives. This effect was observed by the authors [17], whose iron concentration was higher; therefore, the GAC lifetime was shorter. Diclofenac was the most affected by this impact, being the first to achieve the breakthrough instead of clarithromycin. There are two possible causes of this effect. On one side, the higher molar mass of diclofenac disallows it from occupying the clogged pores. On the other hand, the presence of additives in the technical-grade chelating agents could provoke a modification in the GAC charge, thus causing a lower affinity between the material and GAC.

In the case of the UV/H_2O_2 process, using 40 mg L^{-1} of H_2O_2, 52% of the MCs average was removed in the first stage, which is slightly higher than the tests in which citric acid was selected. However, the GAC lifetime extension was closer to using EDDS as a chelating agent, being extended by up to 9 and 13 times for fresh and regenerated GAC, respectively. The increment in GAC lifetime can be caused by the lower COD content from the chelating agent in the water matrix. As reported in the literature, COD competes with MCs in the adsorption process [19,52], reducing the lifetime. In addition to the COD, the presence of iron can also compete with MCs for the adsorption sites, being less adsorbed.

The coupling of processes strengthened the use of regenerated GAC to remove MCs. In almost all the scenarios, the lifetime of regenerated GAC was close to the fresh one. In addition, the regenerated GAC lifetime extension was higher than the fresh GAC in all the scenarios, making it possible to extend it between 2.5 and 13 times. Thus, the approach of coupling the technologies greatly promotes the use of regenerated GAC on a larger scale.

These results, when linked to the previous test with the stand-alone AOP, show that the UV/H_2O_2 process is more suitable than the photo-Fenton process for removing MCs. However, toxicity tests were required to study the possible presence of by-products in the treated water, which could produce a potential toxic release into the environment.

3.4. Toxicity Tests

The toxicity evaluation is highly relevant when working with the AOP, since by-products can be generated and not mineralised in the process. These by-products can be more toxic than the original pollutants [53], obtaining a final effluent with a lower concentration of the selected MCs but more harmful than the untreated water. During the AOPs, three different responses to toxicity can occur: a general decrease in toxicity, an increase in toxicity in the first minutes but a decrease after a determined time, or a general increase in toxicity [54]. Furthermore, it has been demonstrated that the toxicity is not the result of the average of the MC's toxicities; rather, synergetic effects with the matrix take place, affecting the general toxicity [55,56].

Acute toxicity was analysed using the *Daphnia Magna* test; an immobilisation lower than 10% was considered a non-acute toxic sample [55]. No acute toxicity, neither in 24 h nor in 48 h of sample contact, was detected in any of the stand-alone AOP scenarios (Table S7). In the combination of processes, the untreated water showed slight toxicity after 24 h of sample contact in the scenario where EDDS was used as a chelating agent (Table S8), disappearing after 5 min of the photo-Fenton process. In the analysis, after 48 h of sample contact, 20% of immobilised *Daphnia Magna* was reported after 5 min of the photo-Fenton process using technical-grade citric acid. The lower oxidative capacity of the commercial citric acid shown in MCs removal results in a lower capacity for mineralising MCs and releasing degradation by-products. However, the following GAC step significantly reduced that toxicity, with even a value of 0 for the regenerated GAC.

Phytotoxicity was evaluated in the same scenarios and samples as for *Daphnia Magna*. The most sensitive species, principally in germination but also in the root and shoot length, was *Sorghum saccharatum*.

The use of the 40 W LP lamp showed root and shoot length inhibition for *Sorghum saccharatum* (Table S9). The negative effect might be caused by the lower UV dose, which slows down the process, removing partially the MCs, with the possible presence of by-products. Iron:EDDS addition when operating this lamp increased the removal of MCs but had a negative effect on the root and shoot length growth of *Lepidium sativum*. The negative effect of iron:EDDS addition can be caused by the use of EDDS as a chelating agent, which is in agreement with Ahile et al. [47].

The simultaneous use of MP and LP lamps dosing 3 mg L^{-1} of iron (chelated with EDDS) showed no phytotoxic effect in any of the studied species. However, the treatment did not solve the growth inhibition observed in the untreated water. In the case of dosing 1.5 mg L^{-1} of iron (chelated with EDDS), a negative effect was observed in the root and shoot length of *Lepidium sativum* and *Sorghum saccharatum*. The incomplete mineralisation of MCs can explain this due effect to the lower $^{\bullet}OH$ production related to the low concentration of iron:EDDS.

Using 500 W MP lamps with EDDS as a chelating agent achieved satisfactory MC removal results. Regarding toxicity, the best dosage was 5 mg L^{-1} of iron, which generally had a positive effect on the phytotoxicity of all the plant species. The reduction in iron to 3 mg L^{-1} had a slight negative impact on phytotoxicity despite good results for removing MCs. The difference between both scenarios could be associated with the higher amount of iron in the first scenario, entailing a higher amount of EDDS, which was mineralised by $^{\bullet}OH$ [56]. A similar phytotoxicity increment was observed when iron was decreased to 1.5 mg L^{-1} and when H_2O_2 was maintained at 40 mg L^{-1}. In contrast, reducing the H_2O_2 dose to 20 mg L^{-1} did not affect toxicity despite the slowing down of the removal of MCs, which was also observed in the UV/H_2O_2 tests dosing different H_2O_2 concentrations.

The use of analytical citric acid had a positive effect on the stimulation of root and shoot length growth in *Sorghum saccharatum*. This stimulation was higher than when working with EDDS, which is in accordance with Ahile et al. [47], who demonstrated lower phytotoxicity for citric acid. The use of technical-grade iron:citric acid had a negative effect, reducing the stimulation of the growth of *Sorghum saccharatum* and *Sinapis alba*. A possible explanation might be that there is lower $^{\bullet}OH$ production; thus, more by-products were not removed; it could also be because the additives of technical-grade iron which can have phytotoxic effects.

In the tests with UV/H_2O_2, no phytotoxicity effect was observed for *Sorghum saccharatum*. Root and shoot growth were stimulated in the three scenarios for *Lepidium sativum* and *Sinapis alba*, increasing the stimulation percentage as the H_2O_2 dose increased. These results support the previous conclusion, which is that the UV/H_2O_2 process is preferred vs. the photo-Fenton process.

On the coupling of processes, using EDDS as a chelating agent had a negligible effect on the phytotoxicity of *Sorghum saccharatum* (Figure 7). The impact on the other two species was positive, stimulating growth. However, the use of citric acid had a negative effect in both cases, analytical grade or technical grade. The germination rate was reduced, as well as root and shoot length growth. However, only the technical grade had a negative effect on *Lepidium sativum* growth, and it had no effect on *Sinapis alba*. The operation during 5 min of the UV/H_2O_2 process also showed negative effects on *Sorghum saccharatum* root and shoot growth. Thus, the photo-Fenton process using EDDS as a chelating agent was the best scenario when it was operated for only 5 min, and no presence of phytotoxic by-products was observed. This supports the high $^{\bullet}$OH production that not only mineralises the MCs but also degrades the EDDS, removing the toxicity reported by other authors. Nevertheless, the use of EDDS was not an alternative, as it had previously been discarded for scaling up due to the lack of technical-grade products. The GAC filtration showed a positive effect on *Lepidium sativum* and *Sinapis alba* growth, obtaining higher-quality water in all cases. In the case of *Sorghum saccharatum*, no effect was observed for growth. The present results show the usefulness of bioanalytical monitoring with different species in the coupling of processes.

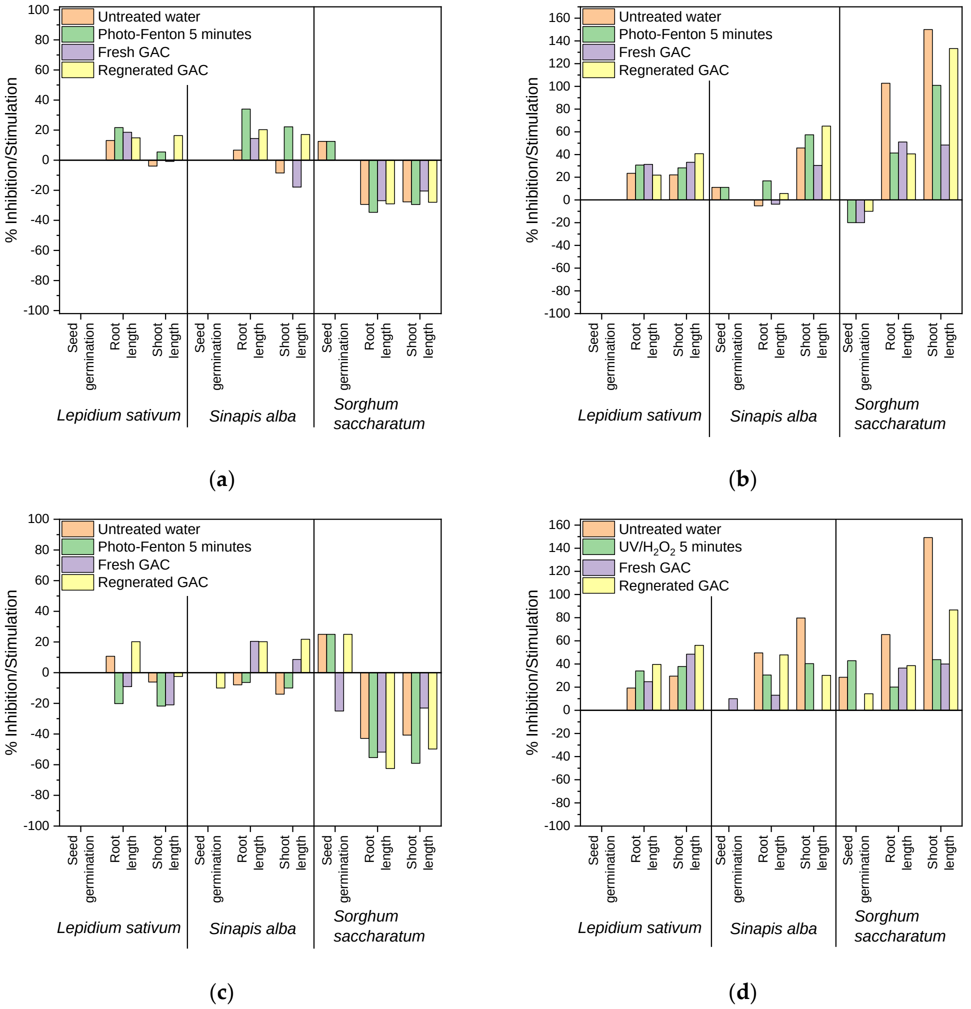


Figure 7. Phytotoxicity inhibition (negative values) and stimulation (positive values) of seed germination and root and shoot length for the three plant species. (**a**) Coupling of the technologies using EDDS as a chelating agent. (**b**) Coupling of the technologies using analytic citric acid as a chelating agent. (**c**) Coupling of the technologies using technical citric acid as a chelating agent. (**d**) Coupling of the technologies using the UV/H_2O_2 process.

4. Conclusions

In this study, the synergies and advantages of coupling different AOPs using lamps as UV sources with GAC filtration was studied. The reduction in reagents for the photo-Fenton process was demonstrated using 1.5 mg L^{-1} iron and 20 mg L^{-1} of H_2O_2 and achieving satisfactory results, which is considerably lower than the reported value for a similar process in the literature. Despite high removal when using the photo-Fenton process, the UV/H_2O_2 process showed slightly lower removal, but the use of iron was avoided. Before the coupling of the technologies, a synergy effect was observed between the AOPs and GAC filtration. Diclofenac was the most recalcitrant MC for GAC filtration but the best removed in the photo-Fenton process. This shows evidence of the advantage of coupling two different quaternary treatments where the most recalcitrant compounds are different for each. Moreover, the coupling reduced the AOP treatment time by between 50 and 66%, consequently reducing energy consumption. Additionally, depending on the scenario, GAC lifetime extension varied between 2 and 11 times, being GAC lifetime comparable when applying the photo-Fenton or UV/H_2O_2 processes. This result showed that UV/H_2O_2 avoided the addition of iron, simplifying the process and operation at natural pH in any case. The coupling of technologies produced a higher positive effect in the regenerated GAC than in the fresh version, obtaining a similar GAC lifetime for both types. Thus, regenerated GAC could be adopted, reducing the carbon footprint, energy consumption, and waste management costs for its disposal. The lack of toxicity highlighted the absence of toxic by-products, as can appear when working with ozone. Further studies will implement the coupling of technologies in an on-site pilot-scale plant in the WWTP of Heiderscheidergrund (north of Luxembourg).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16192824/s1. Table S1: MC recovery rates, relative standard deviations, and limits of quantification; Table S2: Selected GAC main physicochemical properties; Table S3: C/C_0 of the independent MCs in the AOP tests; Table S4: Adsorption characteristics of the selected MCs; Table S5: First-order kinetic model values of stand-alone GAC adsorption; Table S6: 1-(C/C0) of the independent MCs in the adsorption tests; Table S7: Acute toxicity values in AOPs based on *Daphnia Magna* immobilisation; Table S8: Acute toxicity values in the coupling of processes based on *Daphnia Magna* immobilisation; Table S9: Phytotoxicity inhibition (negative values) and stimulation (positive values) of seed germination and the root and shoot length of the three plant species; Figure S1: Microcontaminant removal using the AOP; Figure S2: MC removal using the photo-Fenton process and a 40W LP lamp and 500W MP lamp simultaneously.

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