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# Kinetics of Microcystin-LR Removal in a Real Lake Water by UV/H<sub>2</sub>O<sub>2</sub> Treatment and Analysis of Specific Energy Consumption

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**Abstract:** The hepatotoxin microcystin-LR (MC-LR) represents one of the most toxic cyanotoxins for human health. Considering its harmful effect, the World Health Organization recommended a limit in drinking water (DW) of 1 µg L<sup>-1</sup>. Due to the ineffectiveness of conventional treatments present in DW treatment plants against MC-LR, advanced oxidation processes (AOPs) are gaining interest due to the high redox potential of the OH• radicals. In this work UV/H<sub>2</sub>O<sub>2</sub> was applied to a real lake water to remove MC-LR. The kinetics of the UV/H<sub>2</sub>O<sub>2</sub> were compared with those of UV and H<sub>2</sub>O<sub>2</sub> showing the following result: UV/H<sub>2</sub>O<sub>2</sub> > UV > H<sub>2</sub>O<sub>2</sub>. Within the range of H<sub>2</sub>O<sub>2</sub> tested (0–0.9 mM), the results showed that H<sub>2</sub>O<sub>2</sub> concentration and the removal kinetics followed an increasing quadratic relation. By increasing the initial concentration of H<sub>2</sub>O<sub>2</sub>, the consumption of oxidant also increased but, in terms of MC-LR degraded for H<sub>2</sub>O<sub>2</sub> dosed, the removal efficiency decreased. As the initial MC-LR initial concentration increased, the removal kinetics increased up to a limit concentration (80 µg L<sup>-1</sup>) in which the presence of high amounts of the toxin slowed down the process. Operating with UV fluence lower than 950 mJ cm<sup>-2</sup>, UV alone minimized the specific energy consumption required. UV/H<sub>2</sub>O<sub>2</sub> (0.3 mM) and UV/H<sub>2</sub>O<sub>2</sub> (0.9 mM) were the most advantageous combination when operating with UV fluence of 950–1400 mJ cm<sup>-2</sup> and higher than 1400 mJ cm<sup>-2</sup>, respectively.

**Keywords:** cyanobacteria; cyanotoxins; drinking water; AOPs; hydrogen peroxide; algal bloom; microcystin-LR

**Key Contribution:** UV/H<sub>2</sub>O<sub>2</sub> showed higher kinetics in free MC-LR removal and allowed it to minimize the specific energy consumption operating with UV fluence higher than 950 mJ cm<sup>-2</sup>.

## 1. Introduction

Microcystin-LR (MC-LR) is a hepatotoxin produced by cyanobacteria such as *Microcystis aeruginosa*, *Planktothrix*, *Nostoc* and *Anabaena* and represents one of the most common and most toxic cyanotoxins for human health [1–3]. Cyanobacteria growth is enhanced in the presence of particular conditions such as mild temperature of water (25–35 °C), low flow rates, high concentration of nitrogen and phosphorous [4,5]. Therefore, lakes in areas with a temperate and warm climate represent a perfect habitat for their growth.

Cyanotoxins can interact and alter different parts of human metabolism with consequent effects on health of varying severity. For example, all cyanobacteria genera can produce cyanotoxins belonging to the group of Lipopolysaccharides, which have only a potential irritating effect on the tissues they have come into contact with [6]. On the other hand, the microcystins and nodularins, belonging to the group of cyclic peptides, have the liver as their main target of action being able to cross cell membranes mainly through the bile acid transporter [2,6]. Several studies highlighted the effects on liver tissue in humans exposed chronically to MC-LR [7–9].

The effect of microcystins was also studied by Zhou et al. [10]. They identified that the incidence rate of colorectal cancer was significantly higher in the population who drank water with high concentration of microcystins (e.g., river water) than those who drank tap water [10]. This harmful effect on intestinal cells was also confirmed by subsequent studies [11]. Alosman et al. [12] also pointed out that, aside the liver, MC-LR can cause also cardiogenic complications even if standardized animal models would be needed before the cardiotoxicity of the toxin can be defined with certainty.

The ingestion/inhalation of contaminated water in recreation (e.g., watersports) and, above all, the consumption of contaminated drinking water (DW) represent the main routes of exposure of humans to the toxin [2,6]. The effects due to secondary exposure, such as those due to the presence of MC-LR in plants and vegetables irrigated with water rich in toxins, are also being studied and quantified [13,14].

Considering the harmful effect of MC-LR revealed in literature results, the International Agency for Research on Cancer (IARC) classified this cyanotoxin as possible carcinogenic to humans (Group 2B) [6]. Based on this classification, the World Health Organization (WHO) included the MC-LR within the parameters to be monitored in DW, recommending a temporary limit of  $1 \mu\text{g L}^{-1}$  for total MC-LR (free plus cell-bound) [2]. The European Union implemented this recommendation by including the MC-LR in the revision of the Drinking Water Directive in 2018, providing for a limit of  $1 \mu\text{g L}^{-1}$  [15]. At the current date (15 December 2020) the proposed revision of the directive has not yet been approved so there is currently no unitary legislation at the European Union level about the presence of this toxin in DW.

However, several EU countries where the presence of cyanotoxins within surface water bodies is more widespread have already legislated on the matter providing national limits. For example, in 2012, Italy introduced a limit of  $1 \mu\text{g L}^{-1}$  as equivalent MC-LR referring to the sum of the concentrations of the different microcystins congeners present in DW [16]. In France, in 2001 a decree set the limit of  $1 \mu\text{g L}^{-1}$  for MC-LR in DW [17]. Instead, in 2007, this limit was referred to the sum of the microcystins quantified in the sample [17,18].

Even some non-European countries promoted laws or guidelines in order to minimize the risks for human health related to cyanobacteria and cyanotoxins in DW. For example, Canada established legislative limits for DW, with a seasonal maximum acceptable concentration of  $1.5 \mu\text{g L}^{-1}$  for total microcystins [19], and provided a draft of guidelines for recreational water quality a maximum acceptable concentration of  $10 \mu\text{g L}^{-1}$  for total microcystins [20]. Australia has provided non-mandatory guidelines suggesting that the concentration of total microcystins in DW should not exceed  $1.3 \mu\text{g L}^{-1}$  expressed as microcystin-LR toxicity equivalents [21].

There are two possible approaches to address the problem of the presence of MC-LR in waters: (i) remove the cyanobacteria that produce them or (ii) directly eliminate the free toxin [1]. The conventional treatments present in a drinking water treatment plant (DWTP; e.g., coagulation, flocculation, sedimentation and filtration) allow one to implement the first of the two approaches [22–25]. However, these treatments are not able to remove the MC-LR already secreted by cyanobacteria and present in the water in dissolved form [26]. On the contrary, adsorption on AC is confirmed to be a viable solution for the removal of low molecular weight substances such as cyanotoxins in general and specifically MC-LR [27–29].

Recently, even advanced oxidation processes (AOPs) are gaining interest in the removal of MC-LR due to the high redox potential of the hydroxyl radicals ( $\text{OH}^\bullet$ ) or sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) developed in

the process, which allows one to overcome some limitations given by the limited oxidizing power of other oxidizing agents towards MC-LR, such as  $H_2O_2$  [30,31].

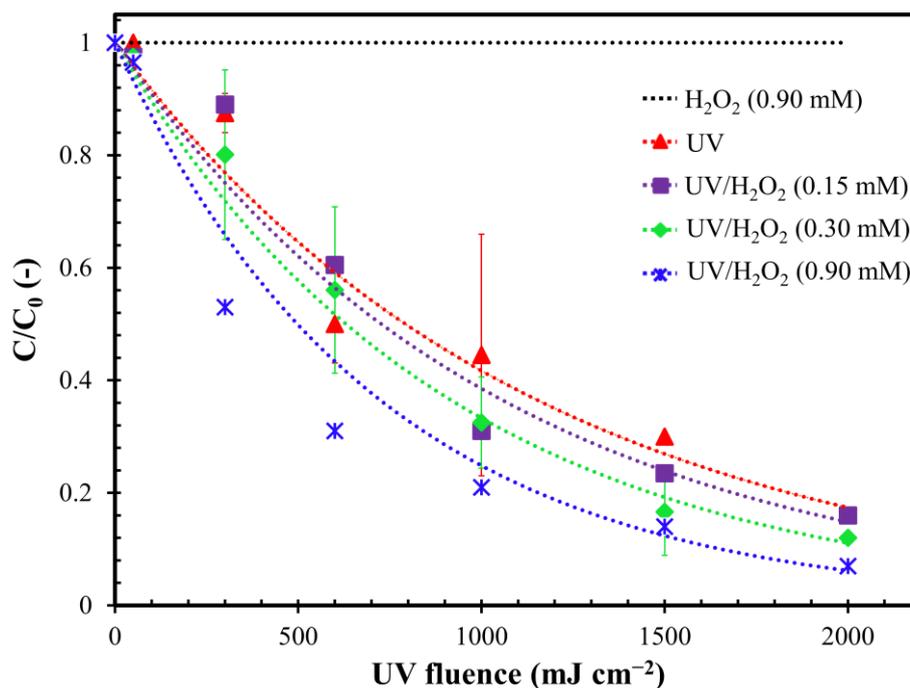
UV/ $H_2O_2$  represents one of the AOPs. The main advantages are given by the absence of chemical sludge production (as opposed for instance to the Fenton process [32]), by the absence of toxic DBPs formation (unlike processes that involve chlorine and ozone [33–36]), and by the great ease of finding the oxidants used (as opposed to processes involving the use of nanostructured metals [37]).

In literature, several examples of application of this process for the removal of MC-LR are reported. UV lamps are used that emit at 254 nm of wavelength [38], close to the wavelength of maximum absorption of the MC-LR (235–238 nm [38,39]) or at 268 nm of wavelength [40]. However, most of the experiments involved the use of synthetic waters, thus only partially evaluating the combined effect of the presence of scavenger substances in the process such as the carbonates. On the contrary, this paper aims to evaluate the effectiveness of UV/ $H_2O_2$  on a real lake water studying kinetics of free MC-LR removal to understand the influence of UV fluence,  $H_2O_2$  dosage and initial MC-LR concentration on the process effectiveness. Moreover, the total specific energy consumption of UV/ $H_2O_2$  for MC-LR removal has been evaluated and compared with UV alone to find the optimal operational conditions.

## 2. Results and Discussion

### 2.1. Effect of the Oxidant

The effectiveness of the  $H_2O_2$ , UV and UV/ $H_2O_2$  processes for MC-LR removal was investigated. Figure 1 shows the degradation of MC-LR as a function of the UV fluence using different oxidants.



**Figure 1.** Degradation of MC-LR as a function of UV fluence in  $H_2O_2$  alone, UV and UV/ $H_2O_2$  processes. The colored curves represent exponential decay curve fitting. Error bars represent the confidence interval ( $n = 3$ ). In case of the  $H_2O_2$  alone treatment, the samples were taken at the time interval corresponding to the same UV fluence of the other tests. Conditions:  $MC-LR_0 = 50 \mu g L^{-1}$ ;  $pH = 7.5$  and fluence rate =  $0.2 mW cm^{-2}$ .

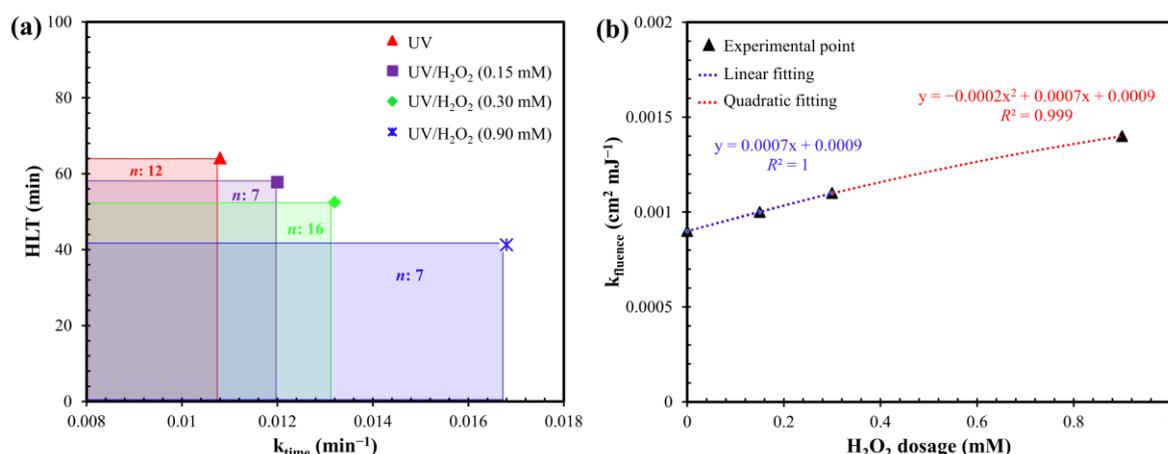
$H_2O_2$  alone did not allow us to remove the toxin even with high contact time. This result is confirmed by Liu et al. [40] who observed an almost absent removal of dissolved MC-LR ( $0.1 \mu M$ ) using  $H_2O_2$  ( $0.1 mM$ ) at  $pH$  nearly 7. On the contrary, the photolysis treatment with UV-C was found to be

weakly effective in removing MC-LR (about 50%), with UV fluence equal to or lower than  $1000 \text{ mJ cm}^{-2}$ . The toxin removal enhanced to 80% using the maximum UV fluence tested ( $2000 \text{ mJ cm}^{-2}$ ).

The UV/ $\text{H}_2\text{O}_2$  combination ensured removal yields higher than 90% with UV fluence equal to  $2000 \text{ mJ cm}^{-2}$  and  $\text{H}_2\text{O}_2$  concentration of 0.9 mM. This result can be attributed to the production of  $\text{OH}^\bullet$  radicals capable of almost completely oxidizing the MC-LR due to their high redox potential [41]. He et al. [38] confirmed the higher effectiveness of UV/ $\text{H}_2\text{O}_2$  with respect with UV alone, obtaining more than 90% of MC-LR removal after  $80 \text{ mJ cm}^{-2}$  of fluence dose ( $\text{H}_2\text{O}_2$ : 1.76 mM) compared to around 20% obtained with UV alone. On the contrary to He et al. study [38], in the present work, a lower MC-LR removal was obtained using the same fluence dose, probably due to the higher initial pH that may have favored the scavenging effect on  $\text{OH}^\bullet$  production [42].

## 2.2. Influence of $\text{H}_2\text{O}_2$ Dosage

The influence  $\text{H}_2\text{O}_2$  dosage on the kinetics of MC-LR removal was studied. As shown in Figure A1 in the Appendix A, all results were well fitted by applying the first-order kinetics model to calculate the MC-LR removal kinetic constants (Figure 2a and Table A1 in Appendix A). As already shown in Figure 1, the  $\text{H}_2\text{O}_2$  dosage generally allowed a better removal yield of the MC-LR. However, this result appeared to be dependent on the concentration of  $\text{H}_2\text{O}_2$  dosed in the reaction. In fact, the UV/ $\text{H}_2\text{O}_2$  combination ensured an efficacy in removing the toxin directly proportional to the quantity of chemical oxidant dosed. The half-life time (HLT) of the MC-LR was reduced from 64.2 (UV alone) to 57.8 min (−10%), 52.5 min (−18%) and 41.3 min (−36%) in the case of UV/ $\text{H}_2\text{O}_2$  (0.15 mM), UV/ $\text{H}_2\text{O}_2$  (0.30 mM) and UV/ $\text{H}_2\text{O}_2$  (0.90 mM), respectively.



**Figure 2.** (a) First-order kinetic constant ( $k_{\text{time}}$ ) and half-life time (HLT) during degradation by UV and UV/ $\text{H}_2\text{O}_2$ . (b) First-order kinetic constant ( $k_{\text{fluence}}$ ) as a function of the  $\text{H}_2\text{O}_2$  dosage. Conditions:  $\text{MC-LR}_0 = 50 \mu\text{g L}^{-1}$ ;  $\text{pH} = 7.5$ ; fluence rate =  $0.2 \text{ mW cm}^{-2}$  and  $n$ : number of data.

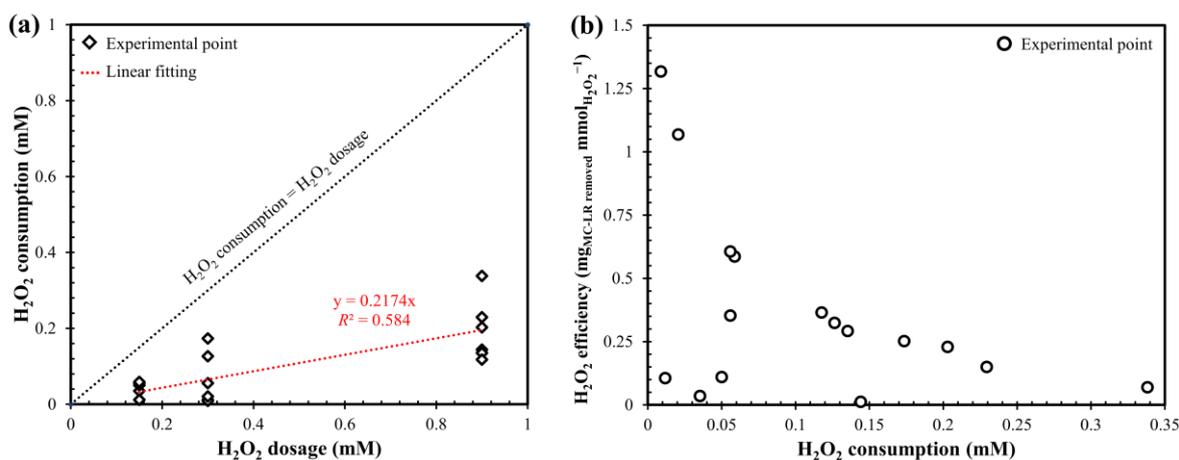
This relation was even more evident by comparing the apparent constant rate of the process (expressed as  $k_{\text{fluence}}$ ) as a function of the  $\text{H}_2\text{O}_2$  dosage. In Figure 2b it can be observed that, for low dosages of  $\text{H}_2\text{O}_2$  ( $\leq 0.3 \text{ mM}$ ), the increase of removal kinetics can be perfectly linearly fitted ( $R^2 = 1$ ). The increase in the kinetics of MC-LR removal was attributable to the increase in  $\text{OH}^\bullet$  production due to the initial higher concentration of  $\text{H}_2\text{O}_2$  as already seen for anatoxin-a removal [43]. This result is in agreement with He et al. [38] who studied MC-LR removal from synthetic DW using UV/ $\text{H}_2\text{O}_2$ . They highlighted that, with initial  $\text{H}_2\text{O}_2$  concentrations below 1 mM, the MC-LR degradation rate constant seemed to increase proportionally with the chemical oxidant concentration following a linear relation [38].

However, considering also a higher  $\text{H}_2\text{O}_2$  dosages (0.9 mM), the best fitting has been obtained with a quadratic function ( $R^2 > 0.99$ ). In fact, when the  $\text{H}_2\text{O}_2$  concentration reached high level (1 mM

for [38] or more than 3 mM for [42]), the production of  $\text{OH}^\bullet$  could be inhibited due to scavenging effect and the removal of MC-LR could remain almost constant or decrease [38,42].

Compared to results obtained by He et al. [38] and Loaiza-González [44], in the present work, lower removal kinetics were obtained using the same concentration of oxidizing agent. This could be related with the presence in the real lake water of higher concentrations of carbonates (Table A3 in Appendix A), which have a high scavenger effect, unlike chlorides and sulphates [38].

Furthermore, the amount of oxidant consumed in the UV/ $\text{H}_2\text{O}_2$  process and the  $\text{H}_2\text{O}_2$  efficiency in removing MC-LR were evaluated. By increasing the initial concentration of  $\text{H}_2\text{O}_2$ , the consumption of oxidant also increased (Figure 3a). This can explain the kinetics detailed in Figure 2b: for constant UV fluence, higher  $\text{H}_2\text{O}_2$  consumption means higher  $\text{OH}^\bullet$  production and therefore higher MC-LR removal. However, as the  $\text{H}_2\text{O}_2$  consumed increased, the removal efficiency of the MC-LR decreased, in terms of MC-LR degraded for  $\text{H}_2\text{O}_2$  dosed (Figure 3b). This result was also observed by m [45] in the application of the UV/ $\text{H}_2\text{O}_2$  for the removal of organic matter and it was attributed to the scavenging effect of hydroxyl radicals that can limit the oxidative power of the process.



**Figure 3.** (a)  $\text{H}_2\text{O}_2$  consumption as a function of  $\text{H}_2\text{O}_2$  dosage. (b)  $\text{H}_2\text{O}_2$  efficiency as a function of  $\text{H}_2\text{O}_2$  consumption. Conditions:  $\text{MC-LR}_0 = 50 \mu\text{g L}^{-1}$ ;  $\text{pH} = 7.5$  and fluence rate =  $0.2 \text{ mW cm}^{-2}$ .

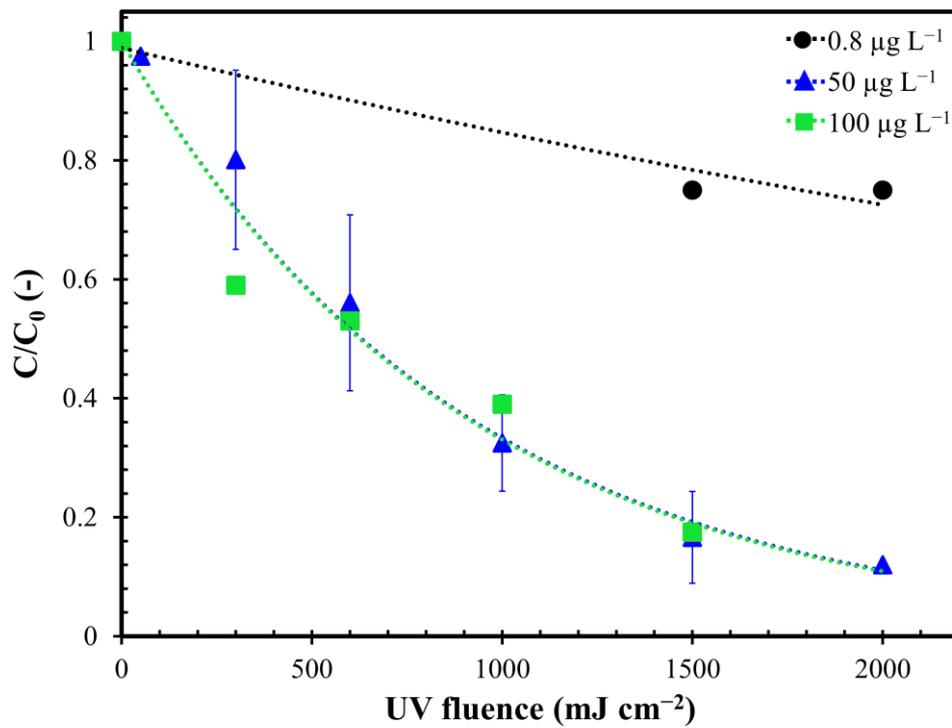
### 2.3. Influence of Initial MC-LR Concentration

Investigations on UV/ $\text{H}_2\text{O}_2$  effectiveness were repeated keeping the  $\text{H}_2\text{O}_2$  dosage constant and varying the initial concentration of MC-LR. The tests were conducted on real water with the addition of MC-LR to obtain a concentration of  $0.8 \mu\text{g L}^{-1}$ ,  $50 \mu\text{g L}^{-1}$  and  $100 \mu\text{g L}^{-1}$ . Increasing the initial MC-LR concentration from  $0.8$  to  $50 \mu\text{g L}^{-1}$ , the removal yields enhanced from 25% to 87.5% (Figure 4). Further increasing the initial MC-LR concentration to  $100 \mu\text{g L}^{-1}$  did not result in an enhancement in toxin removal yields.

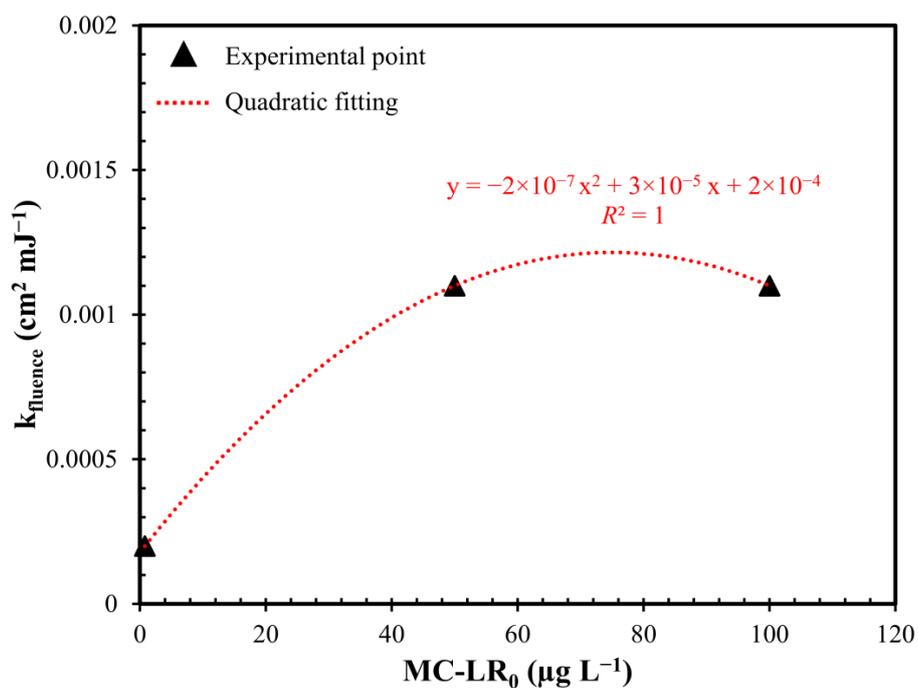
As shown in Figure A2 in Appendix A, all results were well fitted by applying the first-order kinetics model to calculate the MC-LR removal kinetic constants (Table A2 in Appendix A). By increasing the initial concentration of toxin from  $0.8$  to  $50 \mu\text{g L}^{-1}$ , HLT decreased by about 82% (from 288.8 to 52.5 min). The further increase in the initial MC-LR concentration to  $100 \mu\text{g L}^{-1}$  did not lead to a change in the removal kinetics.

Comparing the apparent rate constant of the process as a function of the initial toxin concentration (Figure 5), the experimental points were well fitted by a second degree polynomial function that predicted an increase of MC-LR degradation kinetics when the initial concentration moved from 0 to  $80 \mu\text{g L}^{-1}$ . On the contrary, as the initial MC-LR increased after  $80 \mu\text{g L}^{-1}$ , a lowering of the kinetics of removal was detected. This result was confirmed in the literature by several studies where the lower kinetics, obtained with high MC-LR concentration, are linked to the increase of the internal optical density, which decrease the fraction of light absorbed by  $\text{H}_2\text{O}_2$  limiting  $\text{OH}^\bullet$  production [38,40,42].

On the contrary, with initial MC-LR concentration lower than  $80 \mu\text{g L}^{-1}$ , the obscuration of UV rays can be considered absent.



**Figure 4.** Degradation of MC-LR as a function of UV fluence in UV/H<sub>2</sub>O<sub>2</sub> processes with different initial toxin concentration. The colored curves represent exponential decay curve fitting. Error bars represent the confidence interval ( $n = 3$ ). Conditions: H<sub>2</sub>O<sub>2</sub> dosage = 0.3 mM; pH = 7.5 and fluence rate = 0.2 mW cm<sup>-2</sup>.



**Figure 5.** First-order kinetic constant ( $k_{\text{fluence}}$ ) as a function of the initial MC-LR concentration (MC-LR<sub>0</sub>). Conditions: H<sub>2</sub>O<sub>2</sub> dosage = 0.3 mM; pH = 7.5 and fluence rate = 0.2 mW cm<sup>-2</sup>.

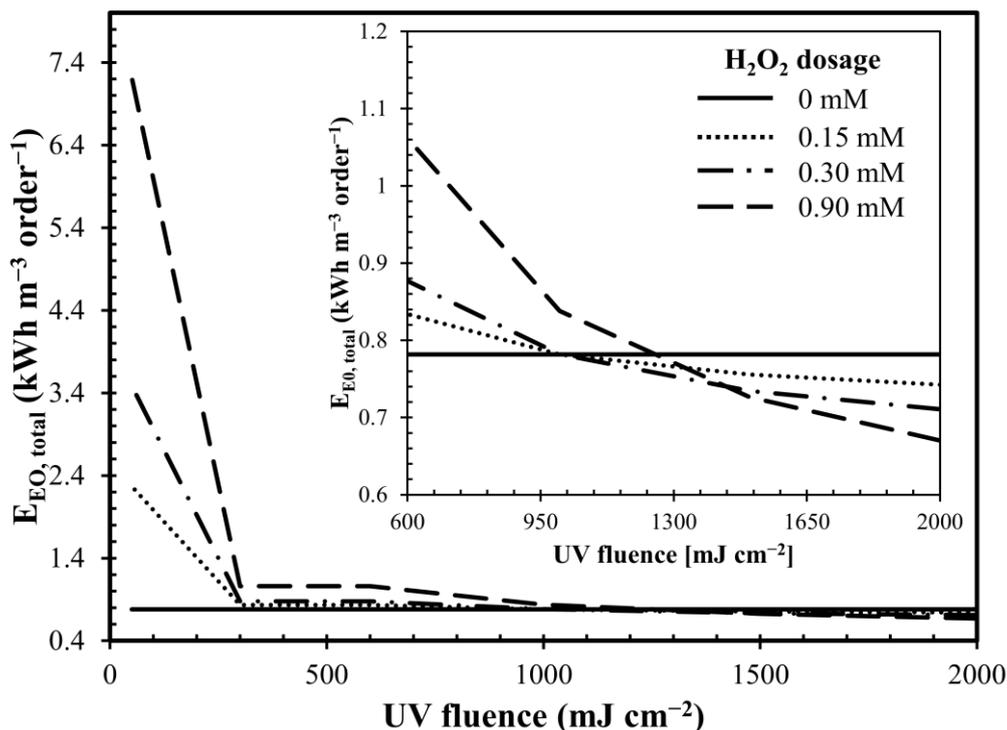
#### 2.4. Energy Consumption

The specific energy consumption required to remove MC-LR by one order of magnitude ( $E_{EO}$ ) was assessed considering both the consumption given by the presence of UV ( $E_{EO,UV}$ ) and the use of  $H_2O_2$  ( $E_{EO,oxidant}$ ). As shown in Figure A3 in Appendix A, electrical energy per order ( $E_{EO}$ ) was reported as a function of  $H_2O_2$  dosage with tested UV fluence.

The results show that the total specific energy consumption ( $E_{EO,total}$ ) followed two different behaviors depending on the UV fluence considered and the  $H_2O_2$  dosed (Figure A4 in the Appendix A). As the dosage of  $H_2O_2$  increased,  $E_{EO,total}$  decreased with high UV fluences ( $1000\text{ mJ cm}^{-2}$ ,  $1500\text{ mJ cm}^{-2}$  and  $2000\text{ mJ cm}^{-2}$ ) while, in the presence of lower UV fluences ( $50\text{ mJ cm}^{-2}$ ,  $300\text{ mJ cm}^{-2}$  and  $600\text{ mJ cm}^{-2}$ ),  $E_{EO,total}$  increased even significantly as the concentration of the chemical oxidant dosed increased (Figure A4 in Appendix A).

In fact, significant  $H_2O_2$  dosages in the presence of low UV radiation did not produce a significant increase in the effectiveness in removing MC-LR. On the contrary, by keeping the  $H_2O_2$  dosage constant and increasing the fluence dose, the removal of MC-LR was more effective due to a greater production of  $OH^\bullet$  radicals. Therefore, the specific energy consumption in relation to the MC-LR removed was lower.

By analyzing the behavior of  $E_{EO,total}$  as a function of UV fluence (Figure 6), the optimal dosage of  $H_2O_2$  that minimized the total specific energy consumption related with MC-LR removed was identified. Operating at low fluence rates (lower than  $950\text{ mJ cm}^{-2}$ ), UV alone allowed it to minimize the  $E_{EO,total}$ . Operating between  $950$  and  $1400\text{ mJ cm}^{-2}$ , UV/ $H_2O_2$  ( $0.3\text{ }\mu\text{g L}^{-1}$ ) combination minimized specific consumption while, for UV fluence higher than  $1400\text{ mJ cm}^{-2}$ , the combination UV/ $H_2O_2$  ( $0.9\text{ }\mu\text{g L}^{-1}$ ) was the most advantageous due to higher MC-LR removal.



**Figure 6.** Total electrical energy per order ( $E_{EO}$ ), by different  $H_2O_2$  dosage, as a function of UV fluence. Conditions:  $MC-LR_0 = 50\text{ }\mu\text{g L}^{-1}$ ;  $\text{pH} = 7.5$  and fluence rate =  $0.2\text{ mW cm}^{-2}$ .

However,  $E_{EO}$  values strongly depend on the removal yields of the toxin and therefore on the production of  $OH^\bullet$  radicals. In addition to the concentration of oxidants used, the production of hydroxyl radicals also depends on many other aspects including the hydrodynamics of the reactor and its configuration [46]. Therefore, a direct comparison with other research is difficult to make. However, although there are not many literature data on  $E_{EO}$  related to the removal of MC-LR and most

of those reported do not evaluate the energetic consumption related to the use of oxidants, the values obtained are of the same order of magnitude as those reported by Schneider and Bláha (2020) [47].

### 3. Conclusions

The kinetics of the UV/H<sub>2</sub>O<sub>2</sub> process was compared with those of UV and H<sub>2</sub>O<sub>2</sub> showing the following result: UV/H<sub>2</sub>O<sub>2</sub> > UV > H<sub>2</sub>O<sub>2</sub>. The UV/H<sub>2</sub>O<sub>2</sub> combination allowed the removal of up to 93% of MC-LR (MC-LR<sub>0</sub>: 50 µg L<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub>: 0.9 mM; UV fluence: 2000 mJ cm<sup>-2</sup> and fluence rate: 0.2 mW cm<sup>-2</sup>). Within the range of H<sub>2</sub>O<sub>2</sub> concentrations tested (0–0.9 mM), the results showed that H<sub>2</sub>O<sub>2</sub> concentration and the removal kinetics followed a quadratic relation. By increasing the initial concentration of H<sub>2</sub>O<sub>2</sub>, the consumption of oxidant also increased but, in terms of MC-LR degraded for H<sub>2</sub>O<sub>2</sub> dosed, the removal efficiency decreased. The initial concentration of MC-LR can significantly influence the kinetics of removal. The results showed that as the MC-LR<sub>0</sub> increased, the removal kinetics increased, up to a limit concentration (80 µg L<sup>-1</sup>) in which the presence of high amounts of the toxin slowed down the process. About the specific energy consumption, UV alone minimized the specific energy consumption required when operating with UV fluence lower than 950 mJ cm<sup>-2</sup>. Operating between 950 and 1400 mJ cm<sup>-2</sup>, UV/H<sub>2</sub>O<sub>2</sub> (0.3 mM) was the most advantageous combination while for UV fluence higher than 1400 mJ cm<sup>-2</sup>, the use of UV/H<sub>2</sub>O<sub>2</sub> (0.9 mM) was the solution that involved lower energy consumption in relation to the quantity of MC-LR removed.

### 4. Materials and Methods

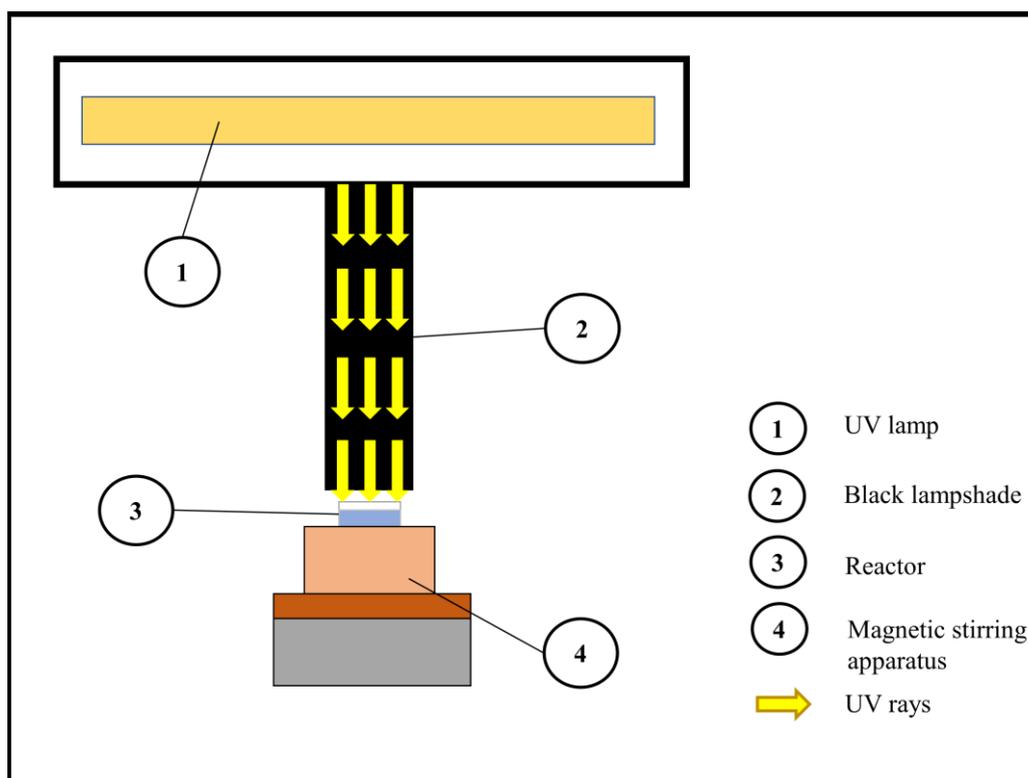
#### 4.1. Water Preparation

In this study, powdered MC-LR (type ALX-350-012-C500; purity ≥ 95%; Enzo Life Sciences Farmingdale, NY, USA) was stored at -20 °C and used to prepare a 50 mg L<sup>-1</sup> solution by adding 10 mL ethanol (≥99.8%) to 0.5 mg powdered MC-LR.

In order to better simulate conditions of treatment of a real DW, raw water was collected from Iseo Lake, in Peschiera Maraglio of Monteisola, in Northern Italy (province of Brescia, Lombardy) at 40 m depth and 40 m from the shore. Characteristics of raw water are reported in Table A2 in Appendix A. To separate dissolved MC-LR from cells, lake water samples were filtered using a 0.45 µm (pore size) glass fiber filter [48,49] and the permeate (MC-LR = 0.1 µg L<sup>-1</sup>) was spiked with the MC-LR solution to obtain toxin concentrations of 0.8 µg L<sup>-1</sup>, 50 µg L<sup>-1</sup> and 100 µg L<sup>-1</sup>. Spiked waters were stored at 5 °C.

#### 4.2. The Lab-Scale System

The batch system used for experimental tests was composed as described in Figure 7. A low-pressure mercury UV lamp, which emits at 254 nm of wavelength, was used. A black lampshade avoided the dispersion of the light beams to the sides and allowed it to concentrate the radiation on the reactor. The intensity of the irradiation given by the UV-C rays incident on the reactor was 0.2 mW cm<sup>-2</sup>. A 50 mL Petri dish (diameter 5.45 cm, height 3.525 cm and thickness 0.25 cm), without lid, was used as a reactor. Inside the reactor, the water (depth 2.60 cm) was kept in constant stirring due to a magnetic stirring apparatus.



**Figure 7.** Scheme of the reactor used in test with UV, H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>.

#### 4.3. Experimental Set-Up and Analytical Methods

This study was carried out testing the following processes:

- H<sub>2</sub>O<sub>2</sub> alone;
- UV alone;
- UV/H<sub>2</sub>O<sub>2</sub> combination.

Tests were conducted at room temperature ( $22 \pm 2$  °C) and aimed to study the kinetics of MC-LR removal and investigate the effects of H<sub>2</sub>O<sub>2</sub> dosage and initial MC-LR concentration.

Hydrogen peroxide (30%, *w/v*) was purchased from Carlo Erba Reagents S.r.l (Cornaredo, Lombardy, Italy) and, during tests, the residual concentration was measured using the triiodide method [50].

Before each experiment, to ensure a stable radiation, the UV lamps were allowed to warm up for 15 min. Fluence rate was measured with iodide/iodate actinometry method [51] and was equal to  $0.2 \text{ mW cm}^{-2}$ .

pH value was monitored by means a portable multiparameter instrument (WTW 3410 SET4, Xylem Analytics Germany Sales GmbH, Weilheim, Germany).

After each fluence interval, samples were collected and catalase from *Micrococcus lysodeikticus* solution (Sigma Aldrich, St. Louis, MO, USA) was used to quench H<sub>2</sub>O<sub>2</sub> reaction in samples before analysis according to Liu et al. [52]. The residual MC-LR concentration was measured with enzyme-linked immunosorbent assay (ELISA) kit, purchased from Eurofins Abraxis (Warminster, PA, USA). LOD and LOQ were equal to  $0.1 \mu\text{g L}^{-1}$  and  $5.0 \mu\text{g L}^{-1}$ , respectively. The treated samples were diluted with Milli-Q water in order to obtain measurable values.

#### 4.4. MC-LR Degradation

The results were elaborated according to a pseudo-first order kinetic as reported in Equation (1) [38]:

$$C = C_0 \times e^{-k_{\text{fluence}} \times F} \quad (1)$$

where  $C_0$  represents the initial concentration of MC-LR and  $C$  is the current  $i$ -th value.  $k_{\text{fluence}}$  represents the apparent rate constant of the process ( $\text{cm}^2 \text{mJ}^{-1}$ ) and  $F$  is the UV fluence ( $\text{mJ cm}^{-2}$ ).  $k_{\text{time}}$  ( $\text{min}^{-1}$ ) was calculated considering the fluence rate of the system ( $0.2 \text{ mW cm}^{-2}$ ), and consequently half-life time (HLT) of MC-LR during treatments was found using the following equation [14]:

$$\text{HLT} = \ln(2) \times k_{\text{time}}^{-1} \quad (2)$$

#### 4.5. Hydrogen Peroxide Consumption

Considering the amount of  $\text{H}_2\text{O}_2$  consumed and the MC-LR removed, the  $\text{H}_2\text{O}_2$  efficiency ( $\text{mg mmol}^{-1}$ ) was calculated according to Equation (3) [45]:

$$\text{H}_2\text{O}_2 \text{ efficiency} = \text{MC-LR}_{\text{removed}} \times \text{H}_2\text{O}_{2\text{consumed}}^{-1} \quad (3)$$

#### 4.6. Energy Consumption

When the concentration of the contaminant is very low, the amount of electric energy required to reduce the contaminant concentration by one order of magnitude can be considered independent of the initial concentration [46,53]. The water depth and the distance between the lamp and the water surface could affect the order of magnitude of the removal [46]. Although the lamp was not submerged into the reactor, in this work these two effects were neglected considering: (i) the low level of water inside the reactor and (ii) the presence of the black lampshade that avoided the dispersion of UV rays conveying them onto the reactor. Therefore, the energy consumption of the UV system was evaluated following the kinetic model of the electrical energy per order ( $E_{\text{EO}}$ ) according to Equation (4) [46,54,55]:

$$E_{\text{EO,UV}} = (P \times t \times 10^3) \times (V \times \log_{10}(C_0 C^{-1}))^{-1} \quad (4)$$

where  $P$  is the nominal power (kW) of the system,  $t$  (h) is the processing time and  $V$  (L) is the volume of water. The nominal power ( $P$ ) was assumed equal to the energy input to the system, considering a fluence rate of  $0.2 \text{ mW cm}^{-2}$  and assuming a UV-C production yield of the lamp equal to 35%.

In view of the application on a larger scale, it is important to know not only the energy consumption necessary to produce UV-C but also the energy consumption due to the dosage of the oxidizing reagent ( $\text{H}_2\text{O}_2$ ). In this work also, the chemical energy consumption associated to  $\text{H}_2\text{O}_2$  was evaluated according to Equation (5) [56]:

$$E_{\text{EO,oxidant}} = (C_{\text{H}_2\text{O}_2} \times \text{CF}) \times (\log_{10}(C_0 C^{-1}))^{-1} \quad (5)$$

where  $C_{\text{H}_2\text{O}_2}$  is the concentration of  $\text{H}_2\text{O}_2$  ( $\text{g m}^{-3}$ ) and  $\text{CF}$  is a conversion factor equal to  $6.67 \times 10^{-3} \text{ kWh g}^{-1}$  [56–58]. Therefore, total energy consumption can be calculated as reported in Equation (6):

$$E_{\text{EO,total}} = E_{\text{EO,UV}} + E_{\text{EO,oxidant}} \quad (6)$$

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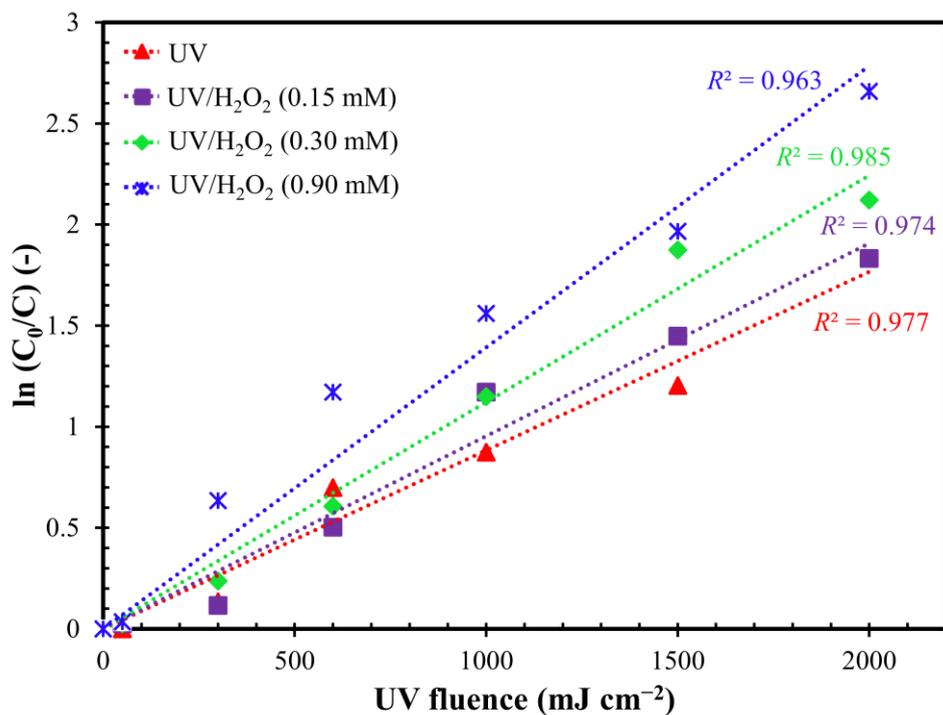
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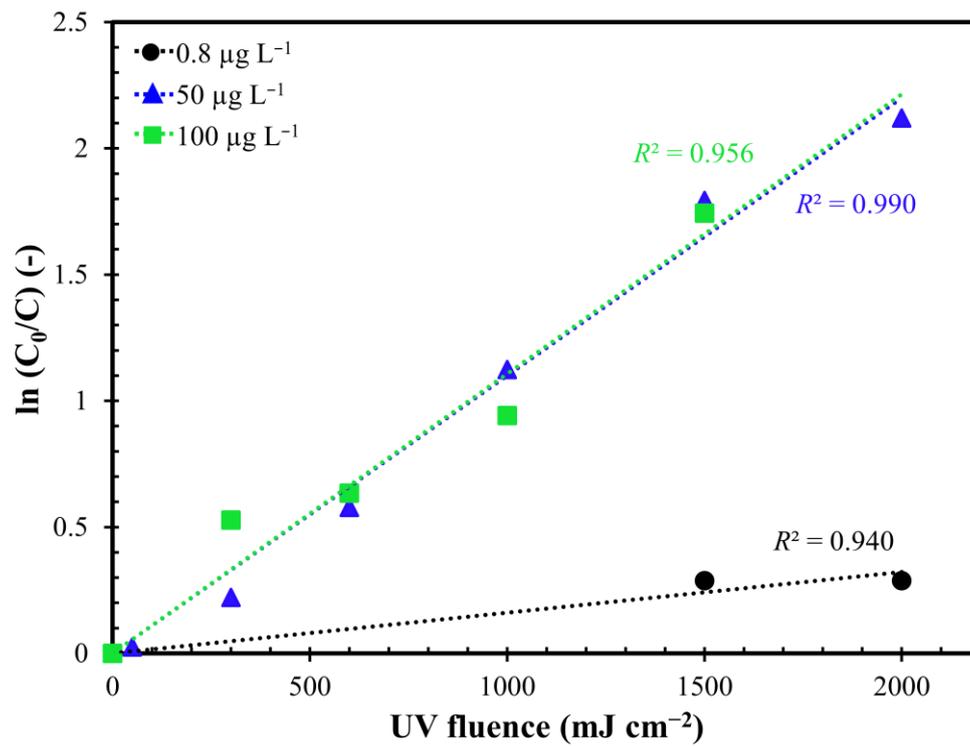
### Abbreviations

AOPs	Advanced oxidation processes
DW	Drinking water
DWTP	Drinking water treatment plant
HLT	Half-life time
IARC	International Agency for Research on Cancer
LOD	Limit of detection
LOQ	Limit of quantification
MC-LR	Microcystin-LR
UV	Ultraviolet
WHO	World Health Organization

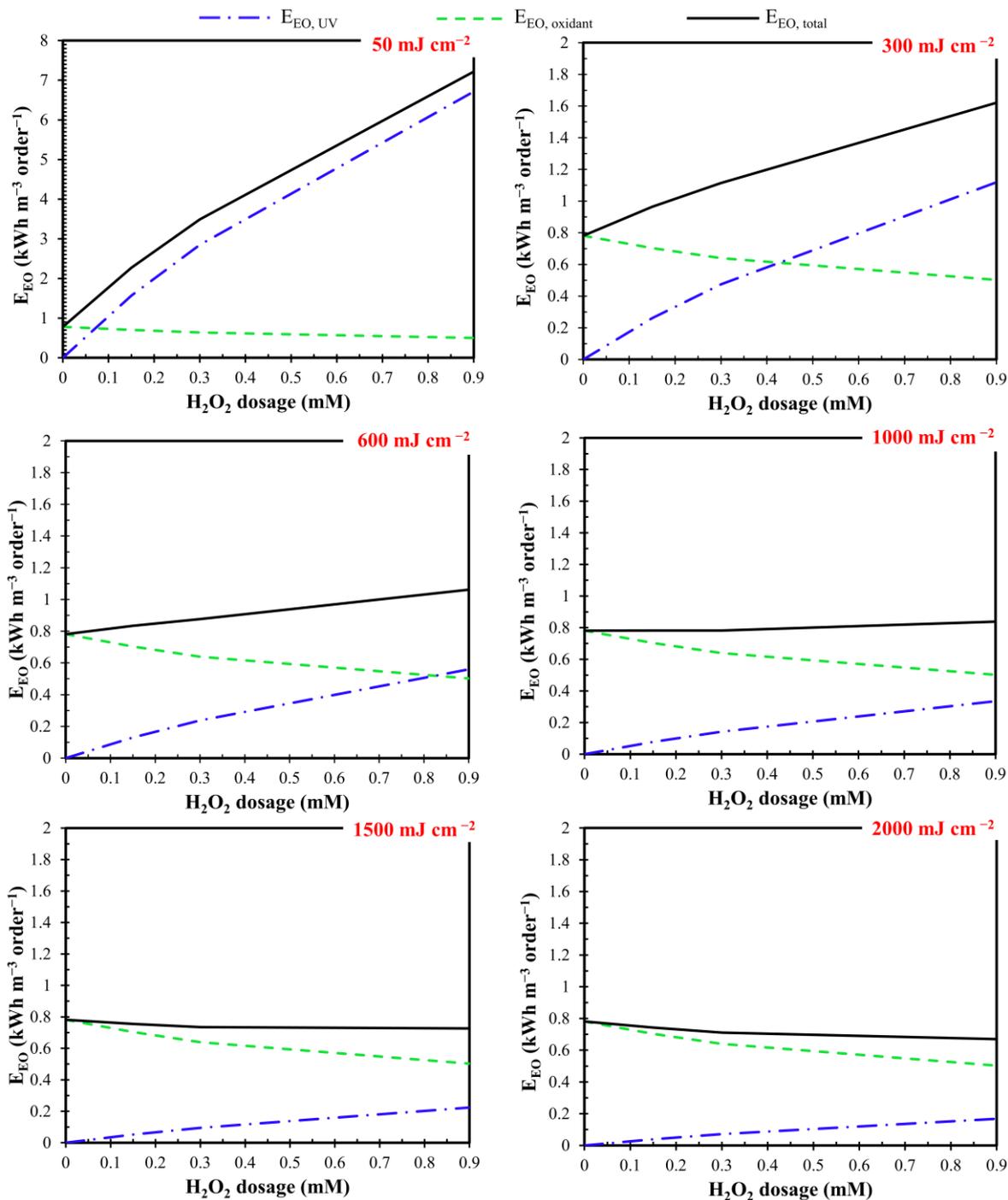
### Appendix A



**Figure A1.** Normalized MC-LR concentration decay following a first-order kinetics model in UV alone and UV/H<sub>2</sub>O<sub>2</sub> processes. The colored lines represented curve fitting. Conditions: [MC-LR]<sub>0</sub> = 50 μg L<sup>-1</sup>; pH = 7.5 and fluence rate = 0.2 mW cm<sup>-2</sup>.



**Figure A2.** Normalized MC-LR concentration decay following a first-order kinetics model in UV/H<sub>2</sub>O<sub>2</sub> processes with different initial MC-LR concentration. The colored lines represented curve fitting. Conditions: H<sub>2</sub>O<sub>2</sub> dosage = 0.3 mM; pH = 7.5 and fluence rate = 0.2 mW cm<sup>-2</sup>.



**Figure A3.** Electrical energy per order ( $E_{EO}$ ) as function of  $H_2O_2$  dosage with different UV fluence. Conditions:  $MC-LR_0 = 50 \mu g L^{-1}$ ;  $pH = 7.5$  and fluence rate =  $0.2 mW cm^{-2}$ .

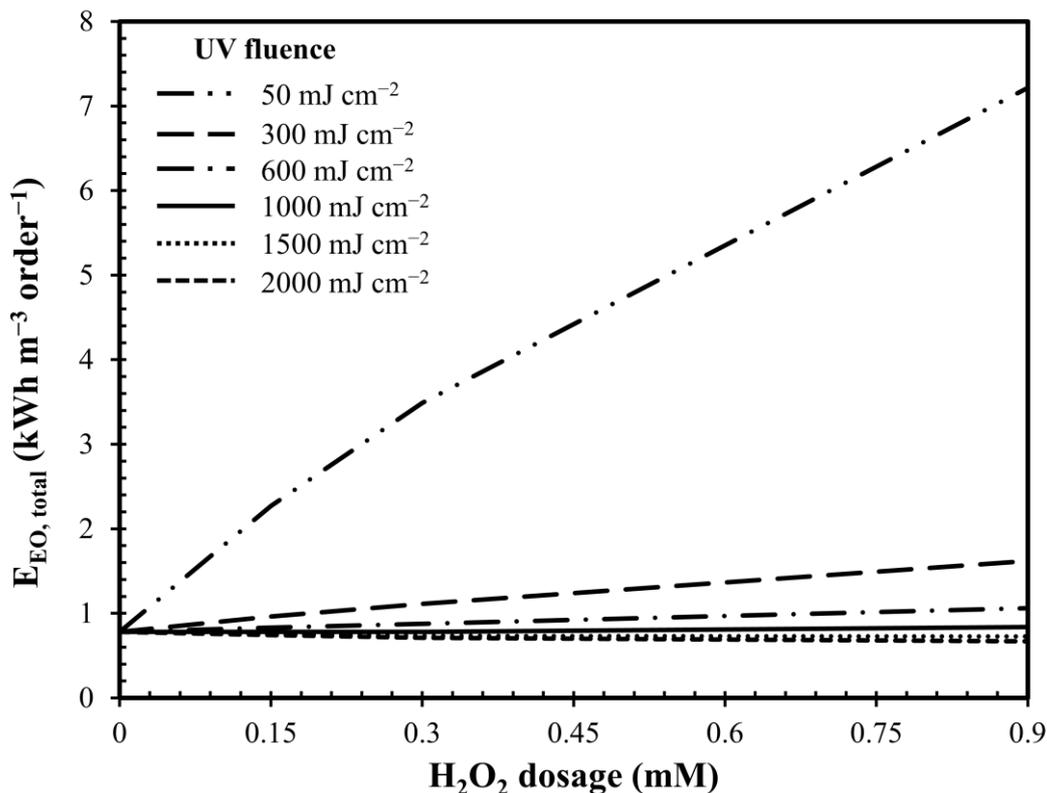


Figure A4. Total electrical energy per order ( $E_{EO}$ ), by different UV fluences, as a function of  $H_2O_2$  dosage.

Table A1. Kinetic constants and half-life times (HLT) of MC-LR during degradation by UV and UV/ $H_2O_2$  using a first-order kinetics model. Conditions:  $MC-LR_0 = 50 \mu g L^{-1}$ ;  $pH = 7.5$ ; fluence rate =  $0.2 mW cm^{-2}$  and  $N =$  number of total data.

	UV	UV/ $H_2O_2$ (0.15 mM)	UV/ $H_2O_2$ (0.30 mM)	UV/ $H_2O_2$ (0.90 mM)
$R^2$ (-)	0.977	0.974	0.985	0.963
$k_{fluence}$ (cm <sup>2</sup> mJ)	0.0009	0.001	0.0011	0.0014
$k_{time}$ (min <sup>-1</sup> )	0.0108	0.0120	0.0132	0.0168
HLT (min)	64.2	57.8	52.5	41.3
$n$ (-)	12	7	16	7

Table A2. Kinetic constants and half-life times (HLT) of MC-LR during degradation by UV/ $H_2O_2$ , with different initial MC-LR concentration, using a first-order kinetics model. Conditions:  $H_2O_2$  dosage =  $0.3 mM$ ;  $pH = 7.5$ ; fluence rate =  $0.2 mW cm^{-2}$  and  $N =$  number of total data.

	UV/ $H_2O_2$ (0.8 $\mu g L^{-1}$ )	UV/ $H_2O_2$ (50 $\mu g L^{-1}$ )	UV/ $H_2O_2$ (100 $\mu g L^{-1}$ )
$R^2$ (-)	0.940	0.990	0.956
$k_{fluence}$ (cm <sup>2</sup> mJ)	0.0002	0.0011	0.0011
$k_{time}$ (min <sup>-1</sup> )	0.0024	0.0132	0.0132
HLT (min)	288.8	52.5	52.5
$n$ (-)	3	16	5

**Table A3.** Characteristics of the raw water before filtration.

Parameter	Unit of Measure	Average Value
pH	-	7.5
Dissolved oxygen	mg L <sup>-1</sup>	9.5–9.7
Turbidity	NTU	2–3
Absorbance UV at 254 nm	1 cm <sup>-1</sup>	0.010–0.020
Suspended solids	mg L <sup>-1</sup>	0–1
Conductivity at 20 °C	µS cm <sup>-1</sup>	260–270
Alkalinity	mg HCO <sub>3</sub> <sup>-</sup> L <sup>-1</sup>	120–130
Bacteria colony count at 22 °C	CFU mL <sup>-1</sup>	80–90
Total coliforms at 37 °C	MPN 100 mL <sup>-1</sup>	65–75
<i>Enterococcus</i>	MPN 100 mL <sup>-1</sup>	2–4
<i>Escherichia coli</i>	MPN 100 mL <sup>-1</sup>	8–10
<i>Pseudomonas aeruginosa</i>	CFU 250 mL <sup>-1</sup>	2–4
<i>Clostridium perfringens</i>	CFU 100 mL <sup>-1</sup>	1–3
Cyanobacterial algae	cells L <sup>-1</sup>	1,700,000–2,000,000
Total algae	cells L <sup>-1</sup>	3,500,000–3,600,000

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