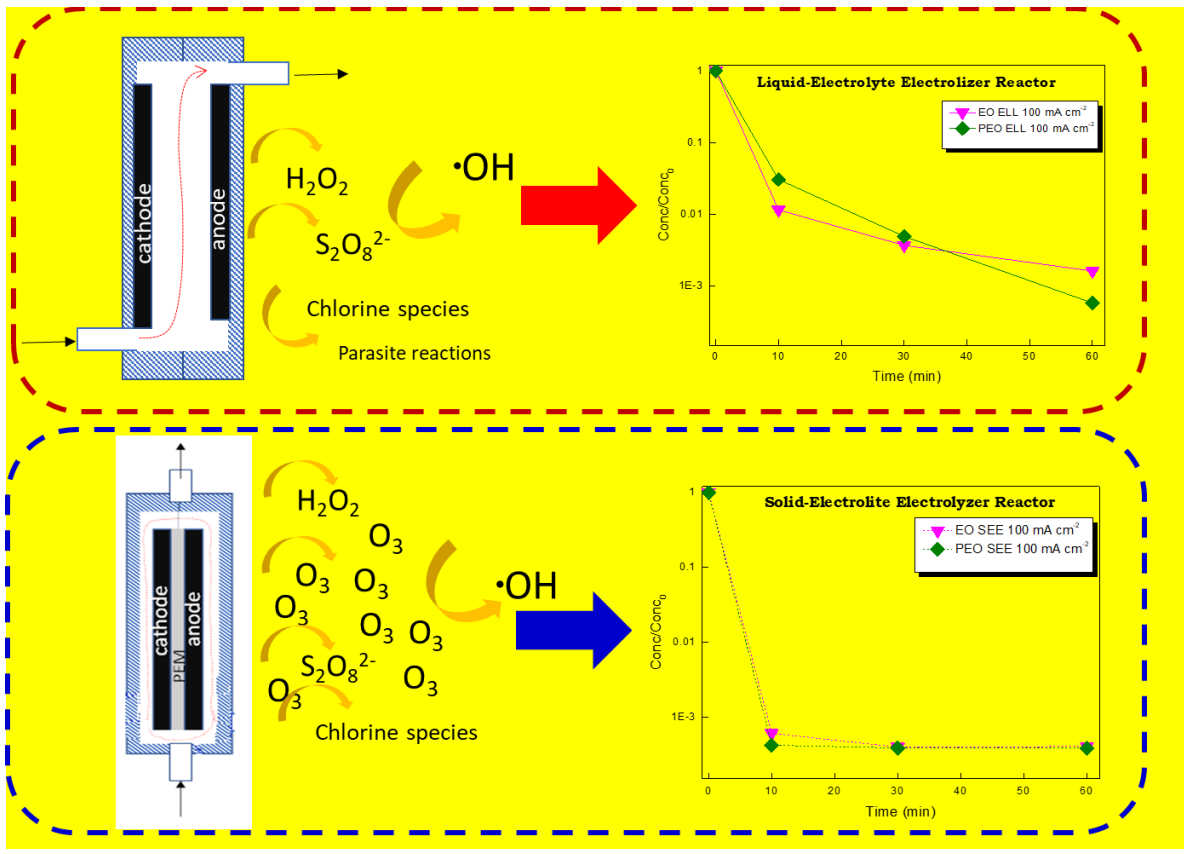1 **Improving the degradation of low concentration of microcystin-LR with PEM**

2 **electrolyzers and photo-electrolyzers**

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8 **Graphic Abstract**

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Abstract

In this work, the performances of two electrochemical cells, a conventional liquid-electrolyte electrolyzer (LEE) and a solid-electrolyte electrolyzer (SEE) were compared for the treatment of two real water matrixes polluted with microcystin-LR at trace concentrations. The first consists of single-compartment flow cell, while the second consists of membrane-electrode assembly flow cell. Both cells can attain the removal of the microcystin, although the toxin degradation was more efficient in the SEE, for both water matrixes assessed, decreasing the initial concentration by 3-logs and achieving in short treatment times concentrations below the guidelines of the World Health Organization (WHO) for drinking water. Irradiation of UVC improves results reached by the electrochemical technologies, although in lower extension than initially expected. The great performance of SEE reactor is attributed to a more suitable production of oxidants and a lower operation-dependence with respect to the water matrix conductivity. This cell can remove pollutants also faster than the single photolysis and, in comparing its performance with the other technologies assessed in this work, it is the best choice requiring the less time and energy to meet the WHO standards, without being necessary the coupling with photolysis.

Keywords

microcystin, algae toxins, hybrid processes, advanced electrochemical oxidation process, electrochemical cells

Highlights

- Microcystins are efficiently degraded by electrolysis and photo-electrolysis
- Microcystin-LR is degraded photochemically by UVC irradiation
- SEE reactor obtained better performance than the LEE for the MC-LR removal

37   •   High dependence of water matrix characteristics when using the LEE

38   •   Irradiation of UVC improved the removal rates in both electrolyzers

39   •   SEE without light irradiation seems to be the best choice for a full-scale

40   application

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1. Introduction

In the last three decades, a very important number of works have been published aiming to elucidate which was the effect of the electrode material on the degradation of hundreds of organic pollutants(Martinez-Huitle et al., 2015; Sirés et al., 2014). General conclusions of these papers indicate that, when using suitable electrodes, such as diamond coatings, all pollutants can be completely mineralized (except for rare molecules such as the reported by this group recently(Mena et al., 2018)) and this fact positioned electrochemical advanced oxidation processes in the crest of the wave of the research in advanced oxidation technologies (Dewil et al., 2017).

However, there is an important drawback of electrochemical processes: efficiency decreases importantly in diluted wastes because the rate of the processes is diffusion-controlled and working with concentrations under $100 \, mg \, dm^{-3}$ of pollutants leads to very inefficient processes. Only when there is a significant contribution of the mediated oxidation processes, the electrolysis becomes interesting, and reaching these conditions is not always easy. These mediated processes are activated by the oxidation of species naturally contained in the water or wastewater to be treated (such as sulfate, chloride, carbonate, etc.) or by special designs of the electrochemical cells made to promote the formation of oxidants such as hydrogen peroxide or ozone (gas diffusion electrodes, membrane electrode assemblies, etc.)(Fernando Perez et al., 2019; Perez et al., 2018a; Perez et al., 2018b; Perez et al., 2019).

One relevant pollutant, typically found at very low concentrations, are the microcystins (MC), which are associated with water polluted with cyanobacteria (Westrick et al., 2010; Wood, 2016). These cyanotoxins belong to a family of hepatocyte cyclic peptides, with

about seventy related compounds, being the two most relevant the microcystin-LR (MC-LR) and microcystin-RR (MC-RR) where L and R represent leucine and arginine, respectively [11-13]. The World Health Organization (WHO) has set 1 µg/L of MC-LR as a guideline value in drinking water (Guidelines for drinking-water quality and criteria and other supporting information. World Health Organization, 1998), whereas recently, the US Environmental Protection Agency (EPA) (Agency, 2020) added three cyanotoxins (microcystin-LR, anatoxin, and cylindrospermopsin) to the Contaminant Candidate List 3 (CCL3) [14,15]. ~~In this context, it is worth to point out that~~ The removal of microcystins is not easy and different methods have been investigated including coagulation (Şengül et al., 2016), pre-oxidation (Gad and El-Tawel, 2015), photocatalytic degradation using TiO$_2$ (Pelaez et al., 2009; Pestana et al., 2015; Yu, 2013), desalination (Boerlage and Nada, 2014; Laycock et al., 2012; Seubert et al., 2012), adsorption (Pavagadhi et al., 2013), application of ultrasounds (Rajasekhar et al., 2012), UV photolysis (He et al., 2013; He et al., 2012; Sharma et al., 2012) and electrochemical oxidation (Shi et al., 2005; Zhang et al., 2009). As pointed out before, this later technology has been demonstrated to be very efficient in the removal of a large variety of compounds, being able to attain their complete degradation. However, the concentrations at which these pollutants are contained in the environment are a serious handicap and the use of new types of electrochemical cells may be the best way to face it.

This work aims to compare the performance of two electrochemical cells in the treatment of organic pollutants contained at very low concentrations: a conventional liquid-electrolyte electrolyzer (LEE) and a solid-electrolyte electrolyzer (SEE). In the first case, the water matrix acts as an electrolyte, while in the second, electrodes are connected to a membrane, which behaves as the main electrolyte of the cell, and then, the system is expected to be less dependent to the water matrix composition. In both cases, the water

95 to be treated is in direct contact with the electrodes and, hence, oxidants can be formed

96 from various of the ions contained (chlorides, sulfates, carbonates, etc.). Because of the

97 relevance of the matrix in terms of the oxidants that can be produced during the

98 electrochemical process, in this work, microcystins are going to be added to two real

99 water matrixes with a very different composition. Thus, because of the low concentration,

100 degradation made by direct electrolysis mechanisms is expected to be negligible as

101 compared to mediated electro-oxidation and, hence, the composition of the electrolyte is

102 expected to be extremely important. Besides, as the production of oxidants is expected to

103 be very important, both cells will be connected to a photolysis system which can also

104 degrade the microcystins or modify the degradation obtained in each of the cells.

105

106 **2. Materials and Methods**

107 **Chemicals and water samples.** Microcystin-LR purity $\geq$ 95% (HPLC) (Enzo Life

108 Science,Inc.), Potassium iodide $\geq$99.99% (Merck), Sodium thiosulfate Reagent Plus®

109 99% (Merck), Starch soluble (Merck), Sulfuric acid 98% (a.r., Scharlab, Spain) are of

110 analytical grade and used as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain)

111 was used for the mobile phase. Double deionized water (Millipore Milli-Q system,

112 resistivity = 18.2 MΩ cm at 25 ºC) was used to prepare all solutions.

113 Fresh waters were directly collected in an agricultural irrigation well and a dump near

114 Ciudad Real (Spain). These water matrixes were subsequently filtered using Whatman®

115 qualitative filter paper grade 1 and used to prepare a standard solution containing 1 mg

116 dm^{-3} of MC-LR. The handling of this toxin was done with extreme care because it is

117 highly toxic and irritant and all the experiments were conducted in a full exhaust cabinet.

118 0.15 dm^3 of each solution was used in each experiment as model wastewater. The initial

119 pH was the natural of each water matrix and no pH correction was performed over the

120 tests. Table 1 shows the characteristics of the water matrixes utilized.

121 **Table 1.** Characteristics of the water matrixes used in the experiments.

Parameter	water matrix 1	water matrix 2
pH	6.3	8.2
Conductivity ($\mu S\ cm^{-1}$)	222	381
F^- ($mg\ dm^{-3}$)	1.22	0.75
Cl^- ($mg\ dm^{-3}$)	20.18	42.99
NO_2^- ($mg\ dm^{-3}$)	0.00	0.00
NO_3^- ($mg\ dm^{-3}$)	0.00	1.10
SO_4^{2-} ($mg\ dm^{-3}$)	40.73	49.06
PO_4^{3-} ($mg\ dm^{-3}$)	17.98	1.61
Na^+ ($mg\ dm^{-3}$)	17.43	27.70
NH_4^+ ($mg\ dm^{-3}$)	0.00	0.00
K^+ ($mg\ dm^{-3}$)	6.99	18.47
Ca^{2+} ($mg\ dm^{-3}$)	23.92	59.03
Mg^{2+} ($mg\ dm^{-3}$)	5.70	14.40

122

123 **Experimental setup.** All the processes were carried out in a lab-scale setup described

124 elsewhere(Souza et al., 2020a), containing 0.15 dm^3 of solution under recirculation. Two

125 electrochemical cells were evaluated in this work. A basic scheme of the concept in which

126 both cells are based is shown in Figure 1. In both cells, anode and cathode were diamond

127 coatings with the same size (approx. 1 cm^2). The first cell was an in-house made single-

128 compartment flow-pass cell in which the electrodes are faced and water pass in the gap

129 between both. The second is a commercial cell (Mikrozon Cartridge supplied by

130 Condias® GmbH (Itzehoe, Germany) and it consists of a membrane electrode assembly

131 (MEA) in which one the faces of the electrodes is in contact with a Nafion ion exchange

132 membrane N324 (DuPont) and the other with the water to be treated. No further details

133 are given because the internal design is protected. Because the direct path between

134 electrodes is the proton-conducting membrane, the main electrolyte of the cell is the solid

135 electrolyte, although water passed throughout the cell also behaves as an electrolyte. In

136 this work, the first concept of cell is going to be called as liquid-electrolyte electrolyzer

137 (LEE) and the second as solid-electrolyte electrolyzer (SEE). Both mini-electrochemical

138 cells were subjected to cleaning procedure during 10 min in a 1 M Na_2SO_4 solution at 0.1

139 A before electrolysis assays.
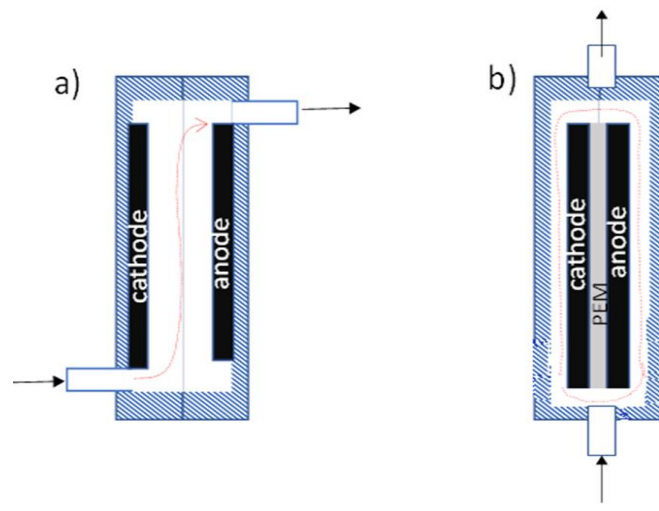
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141 **Figure 1.** Layout of the two electrochemical cells assessed in this work: a) Single-pass

142 flow cell: liquid-electrolyte electrolyzer (LEE) b) single-pass PEM Flow cell: solid-

143 electrolyte electrolyzer (SEE).

144

145 Continuous   recirculation   through   the   reservoir,   UVC   photoreactor   and   the

146 electrochemical cell was kept at a flow rate of 0.78 dm^3 h^{-1}. Before the tests, this solution

147 was homogenized by recirculation through all the units during 10 min in the darkness.

148 During tests, the temperature kept at 20 °C.

149

150 **Analytical procedures.** Samples were taken at different time intervals to monitor the

151 oxidation process. All the samples were filtered with 0.45 µm nylon filters from Whatman

152 before their analysis. MC-LR was determined by HPLC using Mass spectrometry

153 (HPLC/MS/MS). Agilent Technologies 1260 series LC with Agilent Technologies 6460

154 series electrospray ionization triple -quadrupole MS/MS was used. The column was a

155 Poroshell C18 (2.1 mm x 100mm x 2.7 μm). The mobile phase were (A) 0.1% formic

156 acid in methanol and (B) 0.1% formic acid in Milli-Q water. A linear gradient was applied

157 starting at 10% of (A), to 80% of (A) for 3 min over 7 min at flow rate 0.5 mL min^{-1}. MS

158 conditions were: capillary temperature of 350 ∘C, capillary voltage of 4.0 kV, nitrogen

159 gas at flow rates of 12 L min^{-1}. The precursor ion for MC-LR selected was m/z 135 by

160 product ion scan MS/MS mode. Finally, the multiple reaction monitoring (MRM) mode

161 (MZ = 215) was used for obtaining peak areas of the microcystin to track the reaction

162 kinetics. Positive electrospray was employed to record spectra.

163 Total oxidants, pH and conductivity were measured as described elsewhere (Souza et al.,

164 2020a).

165

166 **3. Results and discussion**

167 Figure 2 shows the changes in the MC-LR concentration contained in the Water Matrix

168 1 during the electrolysis (EO) and photo-electrolysis (PEO) with the two electrochemical

169 reactors evaluated in this work. As seen, MC-LR is destroyed by electrochemical,

170 photochemical, and photoelectrochemical technologies and MC-LR concentrations

171 decreased more than three logs in reaction times below 1 hour. Additionally,

172 concentrations reached are below (or in the nearness) the maximum recommended in the

173 guidelines of WHO (1 µg dm^{-3} for microcystin-LR in drinking-water) in all the processes

174 studied. The good degradation results obtained by photolytic treatment can be explained

175 by microcystine structure that contain conjugated double bond and unsaturated bonds

176 responsible to UVC absorption [14] [15][19-21].

During the electrooxidation process employing a LEE reactor, the MC-LR concentration decreases from 1000 µg dm^{-3} down to 10.5 µg dm^{-3} during the first 10 minutes, reaching 1.4 µg dm^{-3} at the end of the treatment with a total specific current charge passed of 0.66 Ah dm^{-3}. In the case of using a SEE type reactor, concentration decreased down to 0.53 µg dm^{-3}, clearly below the guidelines of the WHO, in the first 10 minutes of treatment, with a total required electric charge below 0.1 A h dm^{-3}. This low energy requirement may be easily assumed for a full-scale application.
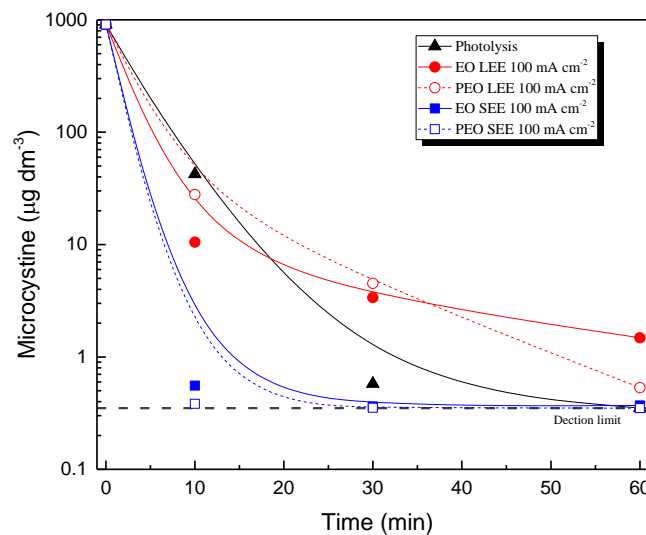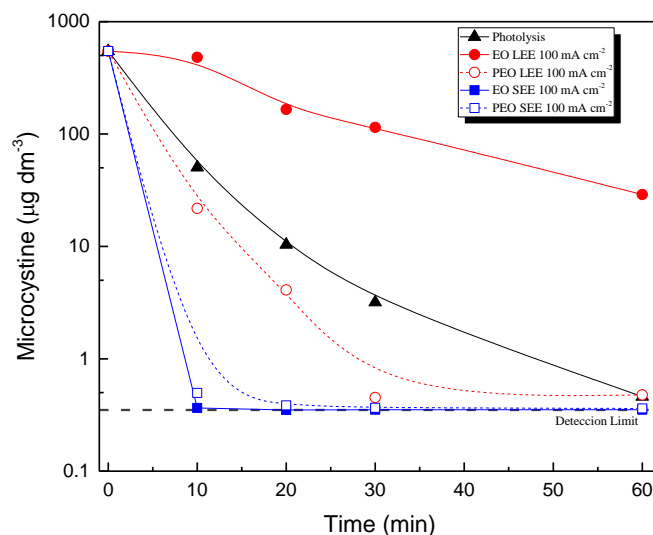

Figure 2. MC-LR concentration reduction (Log scale) as a function of reaction time for all processes studied using LEE reactor and SEE reactor. Conditions: 100 mA cm^{-2}, pH natural, T = 20 ºC without addition of salts. LC-MR solution prepared at Water Matrix 1.

When electrochemical and photolytic treatments are combined, results are improved at long reaction times, but the differences are not as high as pointed out in the removal of other pollutants (Souza et al., 2020b). In fact, at low reaction times, results obtained by the LEE become worse and, comparing to the photolytic process, the concentration obtained by the combined photo-electrolysis with the LEE cell is much worse. Regarding the SEE, the coupling of technologies allows to reach a decrease in the concentration of

194   MC-LR down to 0.36 µg dm^{-3}, just near the detection limit of the measuring technique

195   used.

196   The semilogarithmic plot is not linear in the case of the treatments with the LEE, opposite

197   to what it can be expected in diffusion or mediated oxidation controlled processes(Aquino

198   et al., 2014). In fact, two slopes can be clearly seen, being the second lower than the first.

199   The existence of two slopes in electrochemical and photochemical degradations in

200   discontinuous mode has been associated in the literature(Dionisio et al., 2020) to a change

201   in the oxidation mechanisms. In this case, because of the extremely low concentration of

202   organics, oxidants are expected to explain this change. Regarding to photolysis and SEE-

203   electrolysis, this statement is not as clear as in the case of the photolysis and LEE-

204   electrolysis, considering that the decrease down to the detection limit (0.3 µg dm^{-3}) is

205   almost linear.

206   Figure 3 shows the MC-LR concentration decay when the treatment technologies are

207   applied to the second water matrix. Ionic conductivity of this matrix is higher and there

208   is a higher presence of chloride and sulfate anions, which may become precursors of

209   oxidants species in the reaction media. Because of that, different mechanism reactions

210   may be expected to occur. Here, there are no two slopes in the concentration vs time plot,

211   but only one, fitting well the kinetics to a pseudo-first order, as expected considering that

212   mediated oxidation and diffusion of the pollutants to the electrode surface are controlling

213   the degradation rates.

214

Figure 3. MC-LR concentration reduction (Log scale) as a function time for all processes studied using LEE reactor and SEE reactor. Conditions: 100 mA cm^{-2}, pH natural, T = 20 °C without addition of salts. LC-MR solution prepared at water matrix 2.

218

Regarding the use of LEE, single electrolysis obtained slightly worse results as compared with those obtained with the first water matrix. Same can be said for UCV photolysis, which exhibited a slower removal. However, finally, after one hour of treatment, it reached 99.5 % of elimination, which corresponded to MC-LR concentrations of 0.46 µg dm^{-3}. For electrolysis carried with SEE electrolyser, the MC-LR degradation results show an improvement in this water matrix compared to the water matrix 1. In addition, the combination of photolysis and electrolysis was found to be positive for the two cells studied (also if compared to the bare UVC photolysis). In case of using the LEE reactor, an improvement in the MC-LR removal of 62% was obtained when light was irradiated. However, the best results were obtained with a cell type SEE in which a quick decay is observed with 100 % of elimination (below detection limit of the technique) at 30 minutes for bare electrolysis and at only 10 minutes of treatment for combined photo-electrolysis.

231 Changes in the pH during the treatment of both water matrixes are shown in Figure 4. As

232 seen, changes produced by photolysis are negligible in both water matrixes, which is not

233 the case when electrolysis or photo-electrolysis are applied, for which a decrease in the

234 pH is clearly observed. In addition, changes are more important in the case of the water

235 matrix 1, which can be explained in terms of the lower ionic strength of the matrix and,

236 hence, in its lowering buffering capacity. Because of these changes and considering that

237 pH was not controlled but only monitored, the electrochemical treatment of the water

238 matrix 1 was carried out at acidic conditions while the treatment of water matrix 2 was

239 carried out at more neutral conditions. Worth to highlight that the acidification observed

240 by photo-electrolysis was higher than that observed for the bare electrolysis. As well, the

241 changes in the pH (acidification) are more important when SEE reactor is used.

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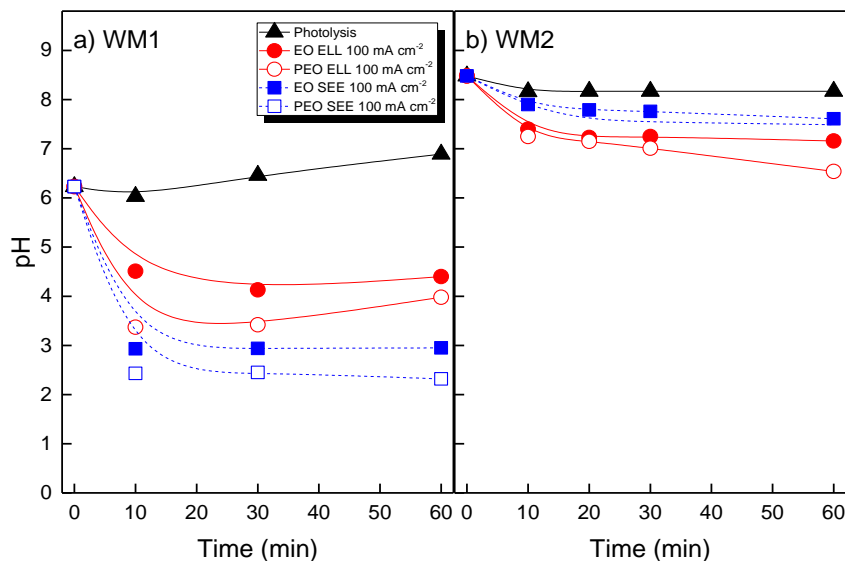
Figure 4. Evolution of pH during the different treatments evaluated in this work

employing a LEE reactor and a SEE reactor. Conditions: 100 mA cm^{-2}, pH natural, T =

20 ºC without addition of salts. LC-MR solution prepared at water matrix 2.

246 Figure 5 shows the oxidants generated during the treatments carried with the two water

247 matrixes. For all technologies the oxidants remaining in the water are quite similar. In

248 fact, the lowest concentrations are observed for the most efficient technologies, because

249 oxidants react and disappear very rapidly, in particular the radical species, and the

250 oxidants measured are those which do not react with the organics and other oxidizable

251 compounds existing in the water matrixes. Comparing the two water matrixes the lowest

252 concentrations of oxidants were obtained for matrix 2, despite of the higher conductivity,

253 and hence the higher concentration of ions which can become precursors of oxidants.

254 Also, important to highlight that oxidants are also produced in a very important way

255 during photolysis, especially in the case of the water matrix 1.

256 This matrix from tap waters contain free available chlorine species ($HClO/ClO^-$) that

257 under UV irradiation are activated generating highly reactive species such as hydroxyl

258 radicals ($HO^.$), chlorine radicals ($Cl^{\bullet}$) and ground-state atomic oxygen ($O(3P)$). These

259 chlorine species (RCS) are responsible to inactivation of MCs [2, 14, 24][22, 23].
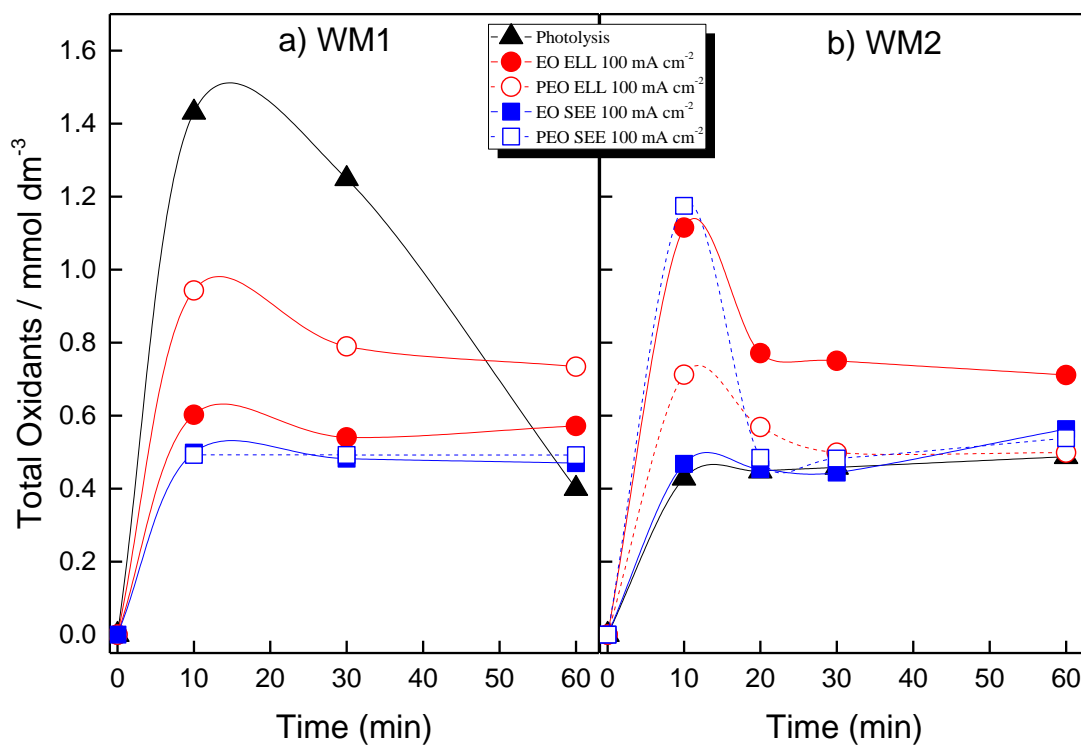
260 In addition, besides direct photochemical degradation, indirect photolysis also can occur,

261 taking in account that in these waters there is a presence of chloride. This reaction occurs

262 through free available chlorine species ($HClO/ClO^-$) that under UV irradiation are

263 activated generating highly reactive species such as hydroxyl radicals ($HO^.$), chlorine

264 radicals ($Cl^{\bullet}$) and ground-state atomic oxygen ($O(3P)$). After the generation of primary

265 radicals ($HO^{\bullet}$ and $Cl^{\bullet}$), they undergo subsequent reactions to produce reactive chlorine

266 species (RCS) mainly $Cl_2^{\bullet-}$ and $ClO^{\bullet}$ as secondary radicals and $O(3P)$ can react with O_2

267 and yield the ozone under oxic conditions [22, 23]. In this way, RCS have demonstrated

268 to be very important oxidants responsible to inactivation of MCs [2, 14, 24]. Zhang et al

269 2018 showed that MC-LR (initial concentration 1.0 mM) was reduced by 20.3% under

270 UV irradiation alone and at a chlorine dose of 3.0 mg L^{-1} and UV fluence of 125 mJ cm$^-$

271 ^{2}, MC-LR was reduced by 92.5%, which was much higher than and 65.1% removal during

272 dark chlorination. Besides, the toxicity of the treated water was reduced by 75.0%, which

14

273 was also higher than 25.7% and 46.7% removal under UV irradiation alone and during

274 dark chlorination, respectively [24].

275 Regarding the electrolysis results, the behavior observed should be explained attending

276 to the differences between the two cells used. While in the LEE the electrolyte is the own

277 water matrix, in the SEE type reactor the electrolyte is the Nafion membrane. In the first

278 case, the generation of hydroxyl radicals and many other oxidants on the diamond surface

279 depends on speciation and quantity of salts in the water matrix. In fact, the cell voltages

280 are higher than those observed in the SEE, especially in the Water Matrix 1, because of

281 the lower ionic conductivity of this matrix. Because of the use of boron doped diamond

282 electrodes, apart from a significant production of hydroxyl radicals, many other powerful

283 oxidants can be formed, such as hydrogen peroxide, ozone and others, such as

284 peroxosalts(Canizares et al., 2009; Moraleda et al., 2019; Velazquez-Pena et al., 2013).

285 Thus, for the LEE, it is expected the production of peroxosulfates from sulfates and

286 chlorine from chloride ions. Under UVC irradiation these species can be activated

287 forming sulfate and chlorine radicals, with a higher oxidation capacity, which can explain

288 that coupling UV-C photolysis to electrolysis improved the MC-LR removal significantly

289 [33, 51-55]. These species can also be formed when oxidants interact among them and,

290 hence, the production of other oxidants such as ozone or hydrogen peroxide is expected

291 to influence on results.

292 In the SEE, oxidants are not only produced on the faces of the electrodes in contact with

293 the water, but they are also produced on the surface that faces the membrane. Thus, it has

294 been demonstrated an important promotion in the production of ozone(Isidro et al., 2019;

295 Isidro et al., 2020; Isidro et al., 2018) in the SEE as compared to LEE. Various studies

296 have concluded that ozone is very effective at much lower concentrations than chlorine

297 and the disinfection occur quite rapidly once a critical residual level is reached [26]. Thus,

298   it is known that mixture of ozone or hydrogen peroxide with peroxosulfate or with

299   chlorine promote the formation of several radicals, which may be the responsible for the

300   much better performance of the SEE system. In addition, when SEE was employed, lower

301   concentrations of surplus oxidants are detected. This means that a significant amount of

302   the oxidants produced in the medium was consumed in the oxidation of microcystin and

303   then, they are not detected in the solution.   However, it is important to consider that the

304   presence of these radicals is not always positive. Lifetime of radicals is very short, and

305   they are only effective when the concentration of organics to be oxidized is high.

306   Otherwise, they are deactivated reactivating the non-radical peroxosalts or forming

307   oxygen and other species with lower oxidation capacity. This can help to understand the

308   two slopes observed in the concentration vs time semilogarithmic decay, with a much

309   lower rate when the concentrations of microcystin are almost negligible and thus, the

310   possibilities of interactions between radicals and pollutants decrease. Other important

311   observation is the pH variation during the experiments. The pH initial of the solution

312   varied more importantly with the SEE reactor. This behavior can explain the better results,

313   once that in according to Farook et al. acidic conditions provided better disinfection than

314   alkaline because of greater ozone stability, and thus higher ozone residuals that can act

315   on the oxidation of MC-LR (Farook, 1977).

Figure 5. Total oxidants generated in Water Matrix 1 (part a) and WM2 (part b) as a function time for different treatments evaluated in this work employing a LEE reactor and a SEE reactor. Conditions: 100 mA cm^{-2}, pH natural, T = 20 ºC without addition of salts.

Figure 6 shows the kinetic constants obtained after fitting the first zone of the experimental degradation results to a first order kinetic model for all experiments carried out in both water matrixes. Regarding to reactors employed, as can be seen, highest rates were obtained when SEE type reactor was employed. This means that the generation of oxidants was huge compared to other oxidants in the LEE reactor. The first order kinetic can be explained because of the pseudo-steady state approach proposed by the group of Palmas (Mascia et al., 2007) and later verified in other works(Aquino et al., 2014; Dionisio et al., 2019a; Dionisio et al., 2019b), which confirm the mediated oxidation as the main mechanisms of oxidation.

The Figure also shows that there was a great improvement in the reaction rate when light irradiation was coupled to EO system, especially when SEE reactor was used. However the effect is not synergistic but antagonistic with values of the synergistic coefficient (calculated according to the procedure describe elsewhere (Souza et al., 2019)) below 1.0, except for the case of the SEE operating in the photoelectrochemical mode, for which a value slightly over 1 is found. Thus, the inset of the Figure shows the synergy index of the combined system which S1 represent the synergism when light irradiation was couple to EO when LEE reactor was used and S2 correspond to UV-C couple to EO-SEE. As can be seen, because of the high efficiency of the single processes and also because of the negative effects of the presence of many radicals when the concentration of organics is very low their combinations do not result in a synergistic but in antagonistic values.
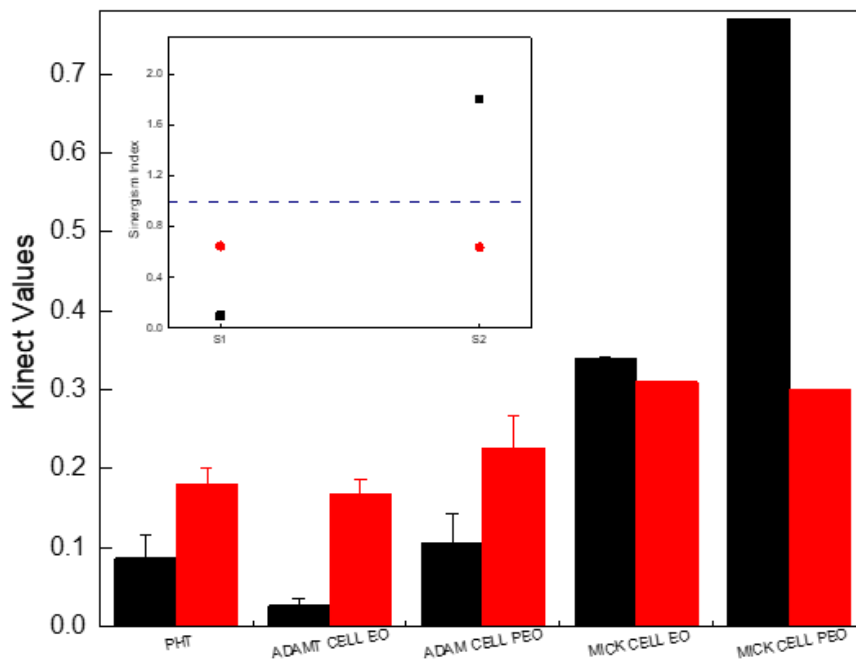

Figure 6. Kinect constants obtained after fitting the experimental degradation LC-MR results to a first-order kinetic reaction model. Inset: Synergistic effect calculated at S1 using processes using a liquid electrolyte electrolyzer (LEE) and a Solid electrolyte electrolyzer (SEE). (■) LC-MR solution prepared at pore water matrix and (●) LC-MR

346 solution prepared at surface water matrix. Conditions: pH natural, T 20 ºC without

347 addition of salts.

348 Hence, important differences are found in the degradation of microcystins associated to

349 the reactor type and light application. Here, it is important to compare the technologies in

350 order to make a first applicability estimation, regardless the TRL of this work is not high

351 enough to make a complete and rigorous economic analysis. This comparison is shown

352 in Figure 7, in terms of the treatment time required and energy consumed by each

353 technology to decrease the concentrations from 1 ppm down to the 1 ppb level

354 recommended by WHO for drinking water.
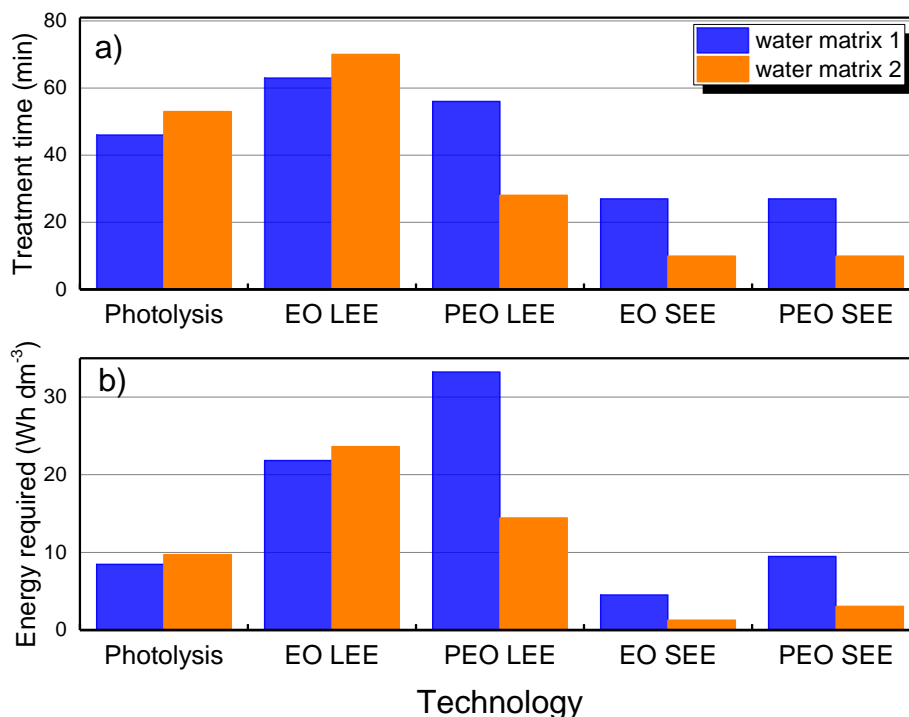
355

356 **Figure 7.** a) Treatment time and b) Energy required by each technology to achieve 1 μg

357 dm^{-3} recommended by WHO for drinking water.

358 Results demonstrate that the selection of a PEM electrolyzer is advisable not only from

359 the point of view of contact times required for the depletion of the hazardous pollutant

360 but also because of the cost, as this system allows to reach the target with the minimum

361 energy demand. In this case the combination with UCV irradiation is not recommended,

362 because despite for the conventional cell (LEE) clear advantages are noticed, in the case

363 of the PEM electrolyzer (SEE) it leads to an unnecessary increase in the energy consumed.

364 The results shown in the Figure, also point out the significance of the water matrix. Thus,

365 in the best case (photo-electrolysis with SEE), energy demanded for the removal of the

366 same amount of MC-LR is more than the double required for a water with higher

367 conductivity (and hence more oxidants precursors).

368

369 **4. Conclusions**

370 From this work, the following conclusion can be drawn:

371 • Microcystin-LR can be destroyed by electrochemical, photochemical and

372   photoelectrochemical technologies. The initial concentration of this toxin can be

373   decreased more than three-logs in less than 1 hour of treatment, attaining values

374   below the recommended in the guidelines of WHO for drinking water (1 μg dm^{-3}

375   ).

376 • Better performances were obtained employing a SEE reactor as compared to LEE

377   reactor for both water matrixes. UCV photolysis was more effective than

378   electrochemical treatment with the LEE but not with the SEE. Combining

379   photolysis with electrolysis leads to improvement in the treatment.

380 • The best results obtained to SEE can be explained in terms of a more suitable

381   production of oxidants. This reactor is also less dependent on the conductivity of

382   the treated water because the main electrolyte is a polymer exchange membrane.

383   •   SEE reactor is the best choice for water treatment with low conductivity and very

384   low pollutant concentration from the point of view of contact times required for

385   your compete depletion as well of the energy required.

386

393

394

395   **5. References**

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