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Influence of the aqueous matrix on the degradation of cyanotoxins by CWPO: A study on the Iberian Peninsula freshwaters

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ABSTRACT

The increasing occurrence of toxic cyanobacterial blooms worldwide represents a critical health and environmental risk. Catalytic wet peroxide oxidation (CWPO) has emerged as an efficient and environmentally friendly technology for the removal of cyanotoxins in water. Nevertheless, its effectiveness has just been demonstrated in deionized water or simple synthetic aqueous matrices. In this work, the effect of the different components of the aqueous matrix on the CWPO of cyanotoxins was deeply evaluated considering the widespread properties of the Iberian Peninsula freshwaters. The presence of Cl^-, HCO_3^- and SO_4^{2-} ions reduced the oxidation rate of cylindrospermopsin (CYN) up to 70–80% at the highest concentrations tested (2000, 250 and 500 mg L^{-1} for Cl^-, HCO_3^- and SO_4^{2-}, respectively) due to their hydroxyl radical scavenging capacity. The presence of natural organic matter (NOM) resulted in a similar outcome (oxidation rate reduction up to 90% at the highest concentration tested, 20 mg L^{-1}), but in this case due to the consumption of hydroxyl radicals in competition with CYN oxidation. The presence of NO_3^- and $H_2PO_4^-$ did not show any significant effect on CYN oxidation. Similarly, the presence of cyanobacteria (*Chrysosporum ovalisporum*, 50 μg chlorophyll-a L^{-1}) did not appreciably affect the CYN oxidation rate. These results were consistent with those obtained by evaluating the impact of real aqueous matrices from drinking water treatment plants (DWTPs) located in Castilla y León and Extremadura regions (Spain) on CWPO performance. This knowledge is key to the implementation of the technology for the treatment of surface waters affected by toxic cyanobacterial blooms.

1. Introduction

Cyanobacteria are one of the oldest groups of living organisms, present in almost every ecosystem on Earth from the poles to hot deserts [1] and especially abundant in freshwaters. Cyanobacteria can play crucial roles in the aquatic environment, as they are involved in relevant ecosystem processes such as the carbon and nitrogen cycles [2]. However, under specific environmental conditions (high temperatures, calm wind, and high nutrient concentrations), massive proliferations of cyanobacteria can arise, leading to dense blooms. In recent decades, the occurrence of cyanobacterial blooms has become an increasingly frequent problem, mainly due to the increasing eutrophication of waters and climate change [3].

Cyanobacterial blooms cause significant alterations in water, affecting its colour, odour, and taste [4]. In addition to these effects, more worrying is their ability to produce highly toxic compounds, the so-called cyanotoxins [5]. Several cyanobacterial taxa can produce cyanotoxins as a secondary metabolite during their cellular metabolism. In fact, it is estimated that most reservoirs in the Iberian Peninsula have suffered toxic cyanobacterial blooms, with more than 35% of them being regularly affected [6]. Cyanotoxins show a diverse chemical nature and exhibit different degrees of toxicity, *i.e.* skin irritation (dermatotoxins), cell damage (cytotoxins), liver damage (hepatotoxins) and nervous system affection (neurotoxins) [7].

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Several works [8–10] have evaluated the efficiency of the conventional processes that are usually present in Drinking Water Treatment Plants (DWTPs) for cyanotoxins degradation. In these studies, it was concluded that the efficiency of the treatments depended mainly on the type of cyanotoxin, the properties of water and the operating conditions, which can vary frequently in a DWTP [8]. Chlorination and physical adsorption demonstrated a successful performance in the removal of microcystin-LR (MC-LR), microcystin-RR (MC-RR) and cylindrospermopsin (CYN), while low efficiencies were found for other important cyanotoxins such as saxitoxin (STX) or anatoxin-*a* (ATX) [8, 10]. Additional disadvantages of these processes are the high doses of activated carbon (100–200 mg L^{-1}) required for the removal of cyanotoxins from water [8] or the occurrence of potentially toxic by-products in the oxidation by chlorine process [11].

In this context, advanced oxidation processes (AOPs) appear as a promising alternative for cyanotoxins degradation in water. Briefly, these processes are defined as oxidation processes based on the *in situ* generation of radicals with high oxidising potential and low selectivity, mainly hydroxyl radicals (HO·), that allow the oxidation of a wide variety of pollutants. Among these, one of the most studied technologies for the degradation of cyanotoxins is ozonation, as it has shown a high removal efficiency on a wide variety of cyanotoxins [12,13]. However, the usual production of multiple toxic by-products is a major disadvantage of this process [8] as well as the need of complex equipment and relatively high energy requirements. On the other hand, photocatalytic processes have been shown to be efficient processes in the removal of cyanotoxins such as ATXs, MC-LR, MC-RR and CYN at laboratory scale [5,14]. However, the dependence on water turbidity, the complex catalyst separation from the treated effluent and the high energetic requirements are limiting factors for the application of these processes [8].

Fenton-based technologies are usually identified as the most cost-efficient AOP [15,16] and have proved to promote a faster cyanotoxin degradation compared to other AOPs like ozonation or UV/H_2O_2 [17, 18]. In particular, the heterogeneous Fenton process, also known as Catalytic Wet Peroxide Oxidation (CWPO), is especially promising as it prevents the production of iron sludge to a high extent and allows to operate under wider pH ranges than the conventional homogeneous system [19]. In our previous contributions [20,21], the feasibility of CWPO promoted by the inexpensive and environmentally friendly catalytic system Fe_3O_4-R400/H_2O_2 proved to be effective for the removal of the most widespread classes of cyanotoxins (MC-LR, MC-RR, CYN, ATX and STX) in deionized water or simple synthetic aqueous matrices.

Despite the benefits of CWPO, practical applications of this technology are limited, mainly due to the complexity of real water matrices. It is well-known that water matrix composition has a direct impact on AOPs performance [22–24]. Natural organic matter (NOM) can consume HO·and promote the fouling catalyst particles and inorganic anions can act as HO·scavengers, leading to an inefficient decomposition of H_2O_2 and thus, reducing the process efficiency and rate [22,25,26]. In this context, a detailed study of each individual component of the aqueous matrix under realistic concentration ranges would allow to understand their influence on the reaction pathway and thus, to optimize the CWPO process for cyanotoxins removal in accordance with of the surface water composition. This work aims to address this challenging issue by considering the varied characteristics of the Iberian Peninsula freshwaters, which are obviously influenced by geographical, climatic, environmental and socio-economic constraints. Fig. 1 shows the different water basins of the Iberian Peninsula. Briefly, freshwater composition is mainly influenced by the geological diversity of the Iberian Peninsula although the role of highly populated areas cannot be overlooked. Argillaceous and calcareous terrains, which are predominant in the eastern part of the Iberian Peninsula, favour a higher content of inorganic dissolved carbon (mainly carbonates and bicarbonates) in water than the siliceous terrains present in the western part of the Iberian Peninsula (median values: 35 mg L^{-1} and 153 mg L^{-1} for the Western and Eastern areas, respectively) (see Fig. S1 of the Supplementary Material for the geological maps). Analyzing the presence of other inorganic species on the Iberian surface waters, a high presence of nitrates (up to 150 mg L^{-1}) has been widely reported in the North-East area. Furthermore, coastal regions exhibit a higher salinity content, mainly chlorides, than inland regions (median values: 130 mg L^{-1} and 44 mg L^{-1} for coastal and inland regions, respectively). Anthropogenic pollution also plays a crucial role in the composition of freshwaters. Accordingly, the presence of sulfate, nitrate and phosphate in freshwater is significantly higher in the vicinity of major urban areas, such as Madrid Region; or in predominantly intensive agricultural regions, such as the Guadiana River and Guadalquivir River basins.

Apart from considering the varied composition of the Iberian Peninsula freshwaters, the impact of the presence of cyanobacteria (*Chrysosporum ovalisporum*, previously known as *Aphanizomenon ovalisporum*) on cyanotoxin oxidation by CWPO was investigated. In the same line, the influence of the oxidation process on cyanobacteria cells was also analyzed. Finally, as a proof of concept, real water samples from the different stages of two DWTPs were also treated in order to determine the optimal stage for the application of CWPO process for cyanotoxins removal during the likely events of cyanobacteria blooms occurrence in

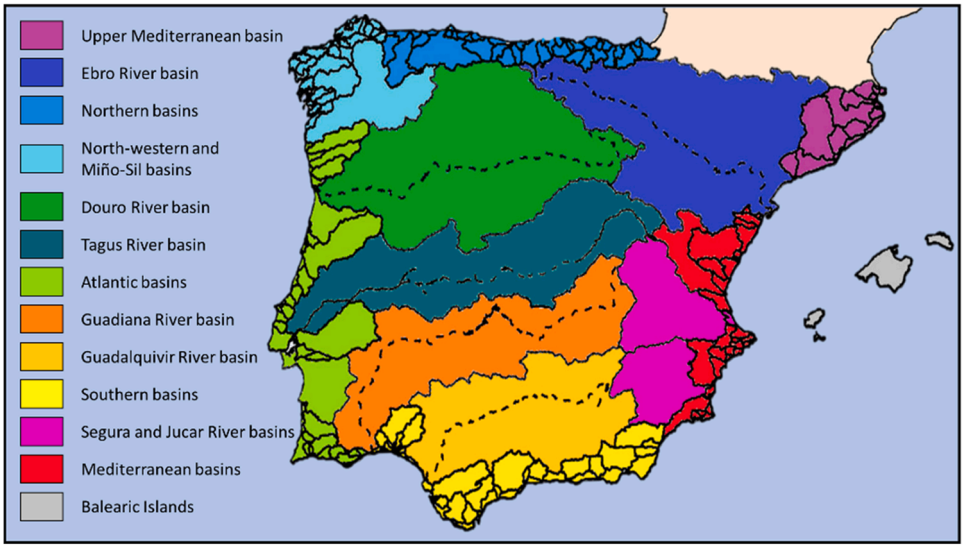

Fig. 1. Water basins of the Iberian Peninsula (adapted from [27]).

surface water.

2. Materials and methods

2.1. Materials and chemicals

CYN (≥99%), MC-LR (≥99%) and MC-RR (≥99%) were provided by Laboratorios CIFGA S.A. (Spain). Hydrogen peroxide solution (33%) (CAS No.: 7722–84–1), sodium biphosphate (≥99%) (CAS No.: 7558–80–7) and sodium nitrate (≥99%) (CAS No.: 7631–99–4) were purchased from Panreac. Nitric acid (65%) (CAS No.: 7697–37–2), sodium bicarbonate (≥99%) (CAS No.:144–55–8) and sodium sulfate (≥99%) (CAS No.: 7757–82–6) were supplied by Scharlau. Sodium chloride (≥99%) (CAS No.: 7647–14–5) and humic acid (CAS No.: 1415–93–6) were obtained from Sigma-Aldrich, respectively. For cyanotoxin quantification, methanol (HPLC grade) (CAS No.: 67–56–1) and acetonitrile (HPLC grade) (CAS No.: 75–05–8) were employed, which were supplied by Scharlau, while acetic acid (≥99%) (CAS No.: 64–19–7) and trifluoroacetic acid (≥99%) (CAS No.: 76–05–1) were purchased from Sigma-Aldrich. All these compounds were used as received without further purification. The magnetite mineral was supplied by Marphil S.L. (Spain) (ref. 50121500). Unless otherwise indicated, deionized water was used to perform all the experiments. The cyanobacterial culture *Chrysosporum ovalisporum* strain UAM292, CYN cyanobacterium producer, was supplied from the culture collection of the Universidad Autónoma de Madrid (Madrid, Spain). Real DWTP influent and effluent samples were obtained from two DWTPs situated in the regions of Castilla y León and Extremadura (Spain), which belong to the Duero and Guadiana basins, respectively. These real aqueous matrices were stored at 4 ºC and analyzed 24 h after being collected.

2.2. Catalyst preparation and characterization

The procedure followed for the preparation of Fe_3O_4-R400 has been previously reported elsewhere [28]. Briefly, powdered magnetite mineral was reduced at H_2 atmosphere (250 NmL min^{-1} of 25 vol% H_2 in N_2) for 3 h at 400 ºC. A detailed characterization of the catalyst, including XRD, textural properties, and magnetic measurements, can be found in previous works [20,28]. Summarizing, the iron content was close to 73% wt., the specific surface area 7 m^2 g^{-1} and the particles showed a mean size of 0.2 μm. On the other hand, the solid showed a crystalline structure, corresponding to the unique presence of magnetite, and strong magnetic properties (81.5 emu g^{-1}). The slight basic character of the material was confirmed by its pH_{PZC} value, close to 8.

2.3. Typical reaction procedure

CWPO experiments were performed under ambient conditions (25 ºC, 1 atm) in a glass batch reactor (20 mL), equipped with a stirrer (750 rpm) and temperature control. In order to avoid possible interferences from ambient light, all experiments were carried out under dark conditions. The initial concentration of cyanotoxin was fixed at 100 μg L^{-1}, the amount of H_2O_2 at 2.5 times the stoichiometric dose for the complete oxidation of the cyanotoxin (1–1.2 mg L^{-1}), the catalyst concentration at 0.2 g L^{-1} and the initial pH was adjusted to 5.0 with nitric acid. These operating conditions were established from a preliminarily experimentation to ensure complete degradation of the cyanotoxins in a reaction time less than 1 h. The evaluation of NOM effect was performed using deionized water fortified with humic acid, whose concentration was related to the total organic carbon (TOC) content. For the experiments carried out in presence of cyanobacteria ($[Chl\text{-}A]_0$ = 50 μg L^{-1}) and in real DWTP waters, the initial concentration of H_2O_2 was increased to 2 mg L^{-1} in order to assure the complete cyanotoxin removal. The initial concentration of the different inorganic ions and humic acid (measured as TOC) were fixed in realistic ranges of concentration based on a study of the freshwaters composition of the main Iberian Peninsula reservoirs (0–2000 mg L^{-1} for SO_4^{2-}, 0–250 mg L^{-1} for HCO_3^-, 0–500 mg L^{-1} for Cl^-, 0–100 mg L^{-1} for NO_3^-, 0–5000 μg L^{-1} for $H_2PO_4^-$ and 0–20 mg L^{-1} for TOC) [29–31]. All experimental data were successfully described by to a pseudo-first-order kinetic model:

$$(-r_A) = -\frac{dC_A}{dt} = k \cdot C_A \cdot C_B \approx k' \cdot C_A$$

Where C_A represents the cyanotoxin concentration and C_B represents the hydrogen peroxide concentration.

2.4. Analytical methods

The evolution of CWPO experiments was followed by periodically withdrawing liquid samples (150 μL) from the reactor (sample times of 5, 15, 30, 45, 60 and 90 min), which were immediately analysed. The catalyst was previously separated using a magnet (less than 10 s were required to achieve the complete separation of the catalyst from the liquid phase). The evolution of cyanotoxins concentration along the oxidation reaction was followed by high performance liquid chromatography, HPLC-UV (Shimazdu, mod. Prominence-I, LC-2030 C LT) using a diode array detector (SPD-M30A). An Eclipse Plus C18 column (150 ×46 mm, 5 mm) (Agilent) was used as stationary phase while the mobile phases were varied depending on the cyanotoxin analyzed. Mixtures of 37/73% and 30/70% (v/v) of acetonitrile and acetic acid aqueous solution (75 mM) were used for the analyses of MC-LR and MC-RR, respectively; while a 2.5% methanol and 0.1% trifluoroacetic acid in water was used for the analyses of CYN. In all cases, the temperature of the column was fixed at 35ºC and the mobile phase flow rate at 0.8 mL min^{-1}. The analyses were carried out at 239 nm for both MC-LR and MC-RR while CYN was measured at 262 nm. Inorganic anions were quantified by ionic chromatography (Metrohm 790 IC) using a conductivity detector. A 3.2 mM Na_2CO_3 aqueous solution was used as mobile phase and a Metrosep A sup 5–250 column (25 cm length, 4 mm internal diameter, 5 μm particle size) as stationary phase. Total organic carbon concentration was measured with a TOC analyzer (Shimadzu TOC V_{SCH}) while a benchtop fluorometer (Moldaenke BBE Algae Analyser) was used for cyanobacteria cells quantification (followed as chlorophyll-*a*, Chl-A, concentration). Light-microscopy images of cyanobacteria were obtained using an Eclipse Ci-S/Ci-L (Nikon) microscope. Fluorescence images were obtained in an Olympus BH-2 epifluorescence microscope (Olympus, Germany) equipped with a Leica DC 300 F digital camera (Leica Microsystems, Germany). The epifluorescence system BH2-RFCA (Olympus, Germany) consisted of an OSRAM Short Arc HBO UV Hg lamp (OSRAM GmbH, Germany), an excitation filter BP545, a dicroic mirror DM570 and an emission filter O590; the result was green light excitation and visualization of red autofluorescence emitted by cyanobacterial pigments phycocyanins and phycoerythrins. For cell counts, 1 mL of diluted culture aliquots were gentle-vacuum filtered through a 25-mm diameter, 0.2-μm pore Anodisc membrane filter (Whatman, England) which were mounted onto microscope slides with a drop of antifading cover-slip medium Aqua-Poly/Mount (Polysciences, Inc., USA). Counts were performed in a minimum of 30 randomly selected fields until reaching statistically significant numbers of counting units and were afterwards referred to the total filtered volume. Dissolved iron concentrations were measured by colorimetry using a Varian Cary 5000 UV–Visible Spectrophotometer following the method of *o*-phenantroline.

3. Results and discussion

As a preliminary step, the degradation of three of the most commonly found cyanotoxins in the Iberian Peninsula (CYN, MC-LR and MC-RR) was studied in deionized water under the previously described operating conditions. Total elimination of the different cyanotoxins was achieved in less than 120 min (see Fig. S2 of the supplementary

material), which is in good agreement with the results presented in our previous contribution [20]. Since the apparent pseudo-first order kinetic constant for these cyanotoxins were quite similar (0.113, 0.061 and 0.149 min^{-1} for CYN, MC-LR and MC-RR, respectively), CYN was selected for the evaluation of the individual effect of each component of the aqueous matrix due to its grater toxicity and higher concentrations in extracellular form compared to MCs [32]. In all cases, Fe leaching represents < 0.2% of the initial catalyst concentration (<0.2 mg L^{-1}). At this dissolved iron concentration, the contribution of the homogeneous Fenton process is negligible. On the other hand, the catalyst stability was demonstrated by performing consecutive reaction runs, finding no significant differences after three cycles (See Fig. S3 of the Supplementary Material).

3.1. Inorganic ions influence

The influence of several inorganic ions commonly found in natural waters (SO_4^{2-}, HCO_3^-, Cl^-, $H_2PO_4^-$ and NO_3^-) was evaluated on the degradation of CYN upon CWPO. The obtained results were successfully described by a pseudo-first order kinetic equation, obtaining correlation coefficients above 0.99 in all cases. The impact of the kind of inorganic ion and its concentration on the apparent kinetic constant value can be observed in Fig. 2.

As can be seen, a clear negative influence on the CWPO rate can be observed when evaluating the presence of SO_4^{2-}, HCO_3^- and Cl^- (Fig. 2a-c), while the presence of $H_2PO_4^-$ and NO_3^- did not imply a significant change in the degradation rate of the cyanotoxin (Fig. 2d-e). The severe interference of Cl^- occurrence in the reaction medium can be attributed to the fact that these anions can act as scavengers of hydroxyl radicals according to the following reaction [26]:

$$HO^{\cdot} + Cl^- + H^+ \leftrightarrow Cl^{\cdot} + H_2O \quad (1)$$

Although chloride radicals are likely to be formed during this reaction, they exhibit a clearly lower oxidizing potential than hydroxyl radicals (1.36 y 2.80 V for $Cl^{\cdot}$ and $HO^{\cdot}$, respectively), thus decreasing the overall degradation rate of the cyanotoxin. This negative interference has been reported in prior works [25,33], where the influence of different ions on the degradation of persistent organic pollutants by AOPs was analyzed. Lipczynska-Kochany et al. [25] demonstrated that the presence of chlorides can cause a decrease in the degradation rate of 4-chlorophenol by the Fenton process. Specifically, they reported a decrease of up to 75% on the degradation rate in presence of 106.5 mg L^{-1} Cl^-. In the same line, Lu et al. [33] also found a remarkable decrease in the degradation rate of aniline through Fenton oxidation for Cl^- concentrations in the range 30–50 mg L^{-1}, achieving the complete inhibition of the reaction at a Cl^- concentration of 7 g L^{-1}. Additionally, it must be noted that, throughout the CWPO reaction in the presence of Cl^-, the appearance of several reaction by-products (not observed while evaluating other ions) was detected. These compounds, probably chlorinated by-products, appeared at initial Cl^- concentrations above 100 mg L^{-1}. Consequently, the generation of these chlorinated by-products would be more probable in brackish waters, where their

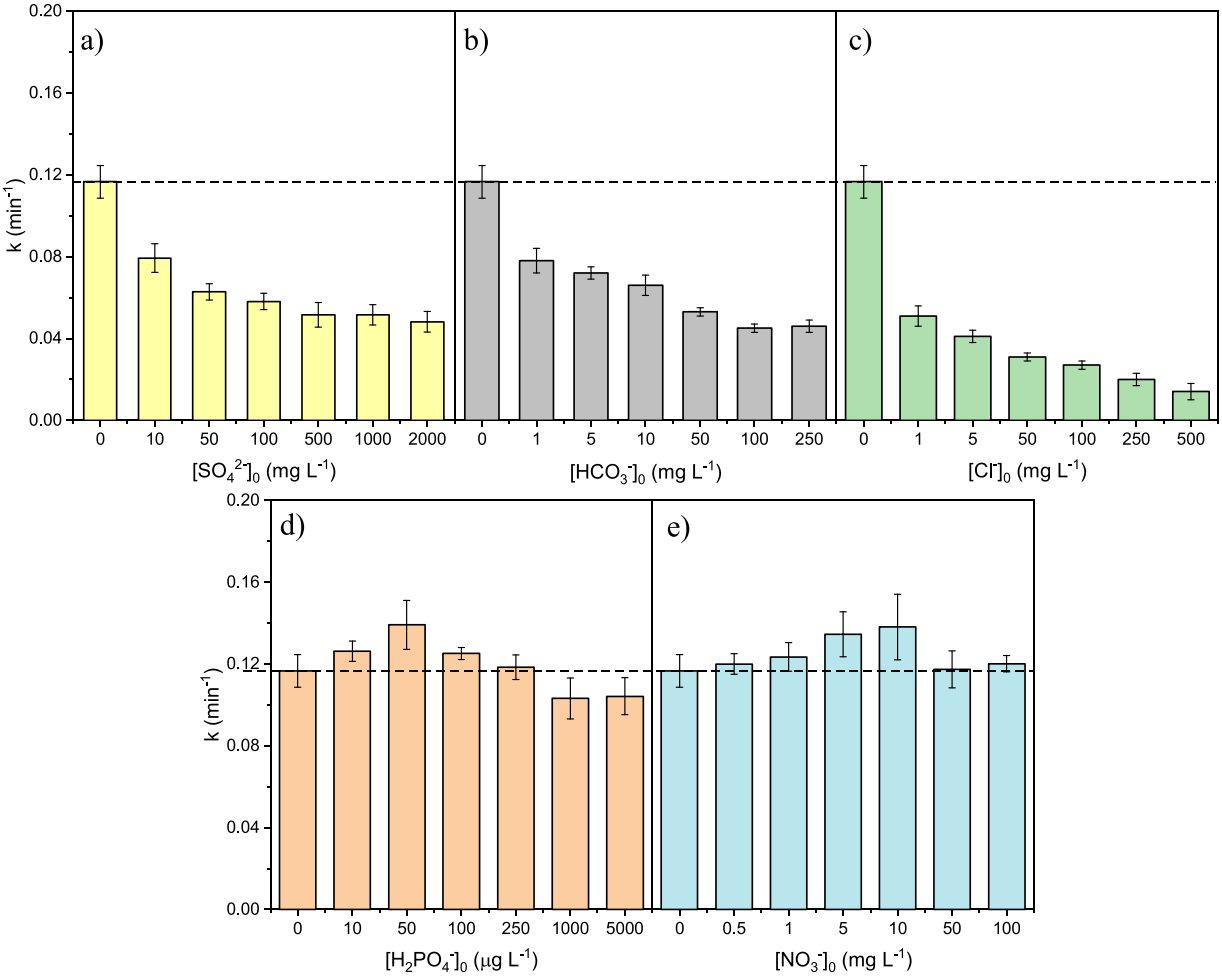

Fig. 2. Apparent pseudo-first order kinetic constant values obtained in the CWPO of CYN as a function of the initial concentration of different co-existing substances in the water matrix: a) sulfate, b) bicarbonate, c) chloride, d) phosphate, e) nitrate. $[CYN]_0 = 100$ µg L^{-1}, $[H_2O_2]_0 = 1$ mg L^{-1}, $[Fe_3O_4\text{-R400}] = 200$ mg L^{-1}, $pH_0 = 5$.

appearance must be carefully considered as organochlorinated species usually present a higher toxicity than the target compound. Due to the high concentration of chlorides in the reaction medium, the presence of these compounds can be explained by the mechanism of CYN degradation by chlorination. Merel et al. [34] established a degradation mechanism in which 5-chloro-cylindrospermopsin was produced as a step prior to the formation of two highly stable compounds. This mechanism explains the different compounds observed in these assays, which were not seen in the presence of other anions.

Similar to the effect of Cl^-, SO_4^{2-} showed an adverse effect on the degradation rate of CYN probably due to its role as hydroxyl radicals scavenger (Eq. 2):

$$HO^{\cdot} + SO_4^{2-} + H^+ \leftrightarrow SO_4^{\cdot-} + H_2O \quad (2)$$

Sulfate radicals exhibit a higher oxidizing potential (2.60 V) than chloride radicals, but also lower than the oxidizing potential of hydroxyl radical. Accordingly, by comparing the effect between Cl^- and SO_4^{2-}, the sulfate anion showed a clearly lower degree of inhibition of the studied reaction. This result is in good agreement with the reported by Siedlecka et al. [35], when evaluating the effect of several inorganic ions (ClO_4^-, Cl^-, SO_4^{2-} and PO_4^{3-}) on the homogeneous Fenton oxidation of methyl tert-butyl ether. When evaluating similar concentrations of these anions, they found that the adverse effect on the reaction rate followed the order $PO_4^{3-} > Cl^- > SO_4^{2-} > ClO_4^-$.

A similar effect was appreciated while evaluating the influence of HCO_3^- since this ion is known to act as hydroxyl radical scavengers like the previous ones. In this case, the mechanism is described by the following reactions [36]:

$$HCO_3^- + HO^{\cdot} \leftrightarrow CO_3^{\cdot-} + H_2O \quad (3)$$

$$HCO_3^- + H_2O_2 \leftrightarrow HCO_3^- + O_2^{\cdot-} + H^+ \leftrightarrow HCO_3^- + HOO^{\cdot-} \quad (4)$$

Besides their role as hydroxyl radicals scavenger, in a recent work it was demonstrated that the radical $CO_3^{\cdot-}$ appears to be the main radical formed along Fenton reaction in solutions containing HCO_3^- at pH> 4 [37]. As $CO_3^{\cdot-}$ (1.53 V) and $HOO^{\cdot}$ (1.70 V) are considerably weaker oxidants than $HO^{\cdot}$, reaction rates are expected to decrease in the presence of carbonates. A similar result was reported by Mingyu et al. [38]. These authors found a slight decrease in the rate of phenol degradation by the homogenous Fenton process due to the presence of these ions. However, the pH of their reactions was fixed to 3, where the form H_2CO_3 is predominant over HCO_3^- and CO_3^{2-} forms so that the inhibitory effect of carbonate at these conditions appears to be less relevant than in the current work. Grebel et al. [39] also studied the effect of carbonates on the degradation of phenol, cyclohexanol and resorcinol along UV/H_2O_2 process at neutral pH. In that work, a decrease up to 50% on the oxidation rate was reported for cyclohexanol, while 30% was obtained for phenol and resorcinol with an initial CO_3^{2-} concentration of 600 mg L^{-1}.

To confirm that the observed decrease in CYN degradation rate can be attributed to a lower effective concentration of hydroxyl radicals, quenching tests were performed in the presence of 2-propanol (1.75 mM), a well-known quenching compound for HO·. Under these conditions, no significant variation in CYN concentration was observed after 5 h of reaction. These results demonstrates that cyanotoxins breakdown is mainly performed by the action of hydroxyl radicals.

Despite the pronounced negative effect obtained by the incorporation of these inorganic ions into the system, remarkably, in all cases, complete CYN degradation was achieved even under the most unfavourable conditions. For instance, reaction times of 60, 75 and 210 min were required to achieve up to 95% CYN degradation under the most unfavourable conditions while evaluating sulfate, bicarbonate and chloride concentration on water, respectively.

On the other hand, from Fig. 2d-e, the occurrence of $H_2PO_4^-$ and NO_3^- had no clear effect on the rate of CYN degradation. This result is in good agreement with the findings described by Pignatello et al. [26]. These authors proved that the presence of nitrates does not interfere with the Fenton reaction. In fact, they recommend the use of salts such as iron nitrate as iron source when performing homogeneous Fenton reactions. Similarly, Pignatello et al. [26] also suggested that phosphate ions can inhibit the homogeneous Fenton reaction through the formation of insoluble complexes with iron, while their interaction with hydroxyl radicals does not interfere the degradation rate. As in this work, a solid iron catalyst was used, this inhibition is not expected, in full agreement with the results obtained.

All in all, despite the clear decrease in the oxidation rate observed in the presence of sulfate, bicarbonate and chloride, CYN conversion values up to 95% were achieved in less than 2 h and pseudo-first order kinetic constant values above 0.025 min^{-1} were obtained. Furthermore, it must be noted that complete degradation of the aromatic by-products detected by HPLC was completely achieved at this CYN conversion value. Only chloride concentrations above 100 mg L^{-1} led to apparent kinetic constant values lower than this threshold value, preventing not only the complete CYN degradation, but also the total removal of the generated aromatics by-products. Among all the reservoirs analyzed in the 2018–2022 period, only around 30% of them presented a chloride concentration higher than this value [29–31], demonstrating the high applicability of the CWPO process. In these situations, an optimization of the CWPO process could be necessary to ensure complete removal of the cyanotoxin in short reaction times, mainly by increasing H_2O_2 concentration.

3.2. Natural organic matter influence

Likewise to inorganic ions, the influence of organic matter occurrence on the degradation of CYN by CWPO was assessed. The apparent molecular weight distribution of the humic acid solution was determined elsewhere [40]. Again, the obtained results were successfully described by a pseudo-first order kinetic equation. Fig. 3 shows the impact of the initial concentration of NOM on the apparent kinetic constant values achieved through CWPO of CYN.

A clearly negative trend in the oxidation rate of CYN was found when increasing the initial concentration of NOM, with the apparent kinetic constant value decreasing up to 90% at the highest concentration of organic matter studied (20 mg L^{-1}). For instance, complete CYN removal was achieved after 180 min with an initial TOC value of 10 mg L^{-1}, whereas the presence of 20 mg L^{-1} of organic matter prevented complete CYN removal after 7 h. It is known that the presence of organic matter can negatively affect various AOPs, mainly due to the sequestration of hydroxyl radicals or light absorption [8,17]. In addition, while evaluating solid catalysts, humic acid may be adsorbed on

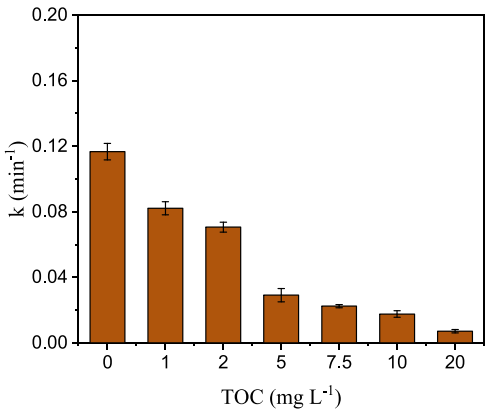

Fig. 3. Apparent pseudo-first order kinetic constant values obtained in the CWPO of CYN as a function of the initial concentration of NOM in the water matrix. $[CYN]_0$ = 100 μg L^{-1}, $[H_2O_2]_0$ = 1 mg L^{-1}, $[Fe_3O_4\text{-R400}]$ = 200 mg L^{-1}, pH_0 = 5.

surface forming a fouling film that inhibit catalyst activity [41]. Accordingly, the adverse effect found in these experiments might be due to the role of humic acids either as hydroxyl radicals scavenger or as a catalyst fouling promoter. Since the used catalyst did not exhibit any increase in carbon content nor a decrease in its surface area, the obtained results suggest that organic matter acts primarily as hydroxyl radicals scavenger. In any case, initial NOM concentrations lower than 7.5 mg L^{-1} allowed to reach a CYN degradation up to 95% in less than 2 h. Around 40% of all the reservoirs (raw water) analyzed in the 2018–2022 period presented a NOM concentration higher than this value [29–31]. As previously mentioned, an optimization of the CWPO process could be then necessary to ensure complete removal of the cyanotoxin in short reaction times, mainly by the use of a higher H_2O_2 concentration. This optimization was performed with real water samples from a DWTP in the last section of this work.

3.3. Cyanobacteria cells influence

One of the possible agents present in the surface waters is cyanobacteria cells. As mentioned above, the probability and intensity of cyanobacterial blooms occurrence has increased dramatically in recent decades [3]. Most toxic cyanobacterial genera may have a considerable proportion of intracellular cyanotoxins and thus, a physical separation process is desirable to ensure the absence of these bacteria throughout the physico-chemical processes of a DWTP. In fact, these plants usually count with different physical systems such as sand filtration, coagulation-flocculation and membrane filtration (including micro-, ultra- and nanofiltration) that allow to remove cyanobacteria cells with a relatively high efficiency (85–99%) [42,43]. Sand filtration allows the separation of cyanobacteria with acceptable efficiency (>85%) and relatively low costs, despite the inconvenience that during filter backwashing it can lead to cell lysis and release of the toxin to water. Coagulation-flocculation process has shown a high separation efficiency (>90% cell removal) at a medium cost, though this method is limited by the highly variable quantities of reagents needed. Membrane filtration seem to be the most efficient technology, with over 98% removal of cyanobacterial cells, though with a relatively high cost. All in all, complete cyanobacteria separation cannot be guaranteed and thus, it is essential to analyse the fate of cyanobacteria cells upon the oxidation treatment proposed in this work.

For this purpose, CYN degradation in the presence of one of its most widespread cyanobacterial producers, *Chrysosporum ovalisporum*, was evaluated. The concentration of cyanobacteria was estimated by measuring chlorophyll-*a*, a standard proxy for phytoplankton biomass in general. An initial concentration of 50 μg Chl-A L^{-1} was selected, which is equivalent to an established cyanobacterial bloom with high biomass. Furthermore, this is the threshold value included in the Spanish Royal Decree 3/2023 [44] for the compulsory control of cyanobacteria and cyanotoxins identification in water reservoirs intended for water consumptions. Experiments were carried out at almost the same operating conditions above mentioned, varying the initial concentration of H_2O_2 from 1 to 2 mg L^{-1} as cyanobacteria cells are expected to compete for the consumption of hydroxyl radicals.

As can be observed in Fig. 4, cyanobacteria occurrence did not negatively affect CYN degradation rate by CWPO. The obtained results were still successfully fitted by a pseudo-first order kinetic equation. In fact, the apparent rate constant value remained practically unchanged when cyanobacterial cells were present in the reaction medium at the concentration level used in this work. These results seem to indicate that the release of cyanotoxin *via* cell disruption occurs at a significantly lower rate than cyanotoxin oxidation. To evaluate the possible modifications suffered by the cyanobacterium throughout the CWPO process, optical and fluorescence microscopy images of the initial and final reaction samples were obtained (Fig. 5).

As can be seen in Fig. 5 (see Fig S4 of the supplementary material for optical microscopy images), the initial sample submitted to CWPO

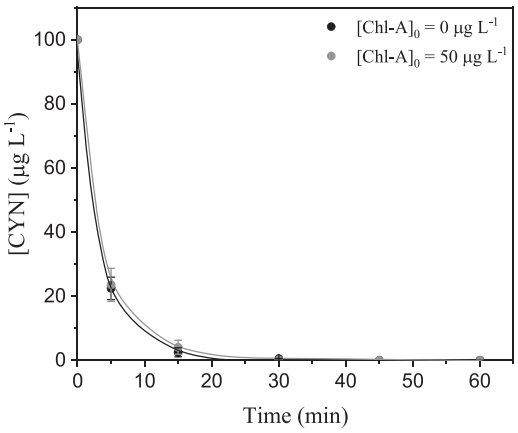

Fig. 4. Effect of the presence of cyanobacteria (Chrysosporum ovalisporum) on the CWPO of CYN. $[CYN]_0 = 100$ μg L^{-1}, $[H_2O_2]_0 = 2$ mg L^{-1}, $[Fe_3O_4\text{-R400}] = 200$ mg L^{-1}, $pH_0 = 5$.

contained a multitude of filaments formed by a large number of cells, typical of *Chrysosporum ovalisporum* [45] in a healthy state (the reddish colour represents a high the auto-fluorescence of the cyanobacterial pigments phycobiliproteins). In contrast, after the CWPO treatment, cyanobacteria filaments could hardly be seen in the microscopy images finding that the number of cells per filament was also substantially decreased. Consistent with these observations, the number of healthy cyanobacteria filaments after the treatment was practically negligible. From these images, the number of viable cells before and after the CWPO process was counted, showing a decrease of more than 97% of viable cells. This result is consistent with the high decrease in cyanobacterial biomass (expressed as Chl-A) observed, achieving up to 95% of Chl-A elimination.

From these results, it can be concluded that the presence of a relatively high concentration of cyanobacteria in the water matrix does not imply a counterproductive effect on the cyanotoxin oxidation rate. Furthermore, although an increase in cyanotoxin concentration could be expected at short reaction times as a result of cellular lysis and consequent intracellular toxin release, this effect was not observed clearly indicating that the degradation rate of the cyanotoxin is higher than the rate at which it is released into the liquid phase. To further explore this effect, an additional experiment was carried out in the absence of commercial cyanotoxin. In this assay $[Chl\text{-}A]_0 = 100$ μg L^{-1} (Fig. S5 of the Supplementary Material), a slight increase in extracellular concentration was observed after 5 min of treatment, disappearing after 15 min. This assay suggests that the CWPO process is capable of efficiently degrading the extracellular cyanotoxin produced after cell lysis. This promising result differs from the results usually reported in the application of other oxidative processes where a high increase in cyanotoxin concentration caused by cellular lysis is commonly detected. Fan et al., (2014) and Li et al., (2022) [46,47], evaluated the application of different conventional oxidation treatments for the simultaneous elimination of *Microcystis aeruginosa* and MC-LR. These authors demonstrated a high efficiency in the inactivation of the cyanobacteria using Cl_2 (5 mg L^{-1}, 30 min), $KMnO_4$ (10 mg L^{-1}, 180 min) and O_3 (8 mg L^{-1}, 30 min) as oxidants. During those reaction times, they observed a significant increase in concentration of MC-LR throughout the reaction due to cellular lysis. For instance, Fan et al. [46] reported increases in the extracellular fraction of MC-LR of up to 63% during the chlorination process ($[Cl_2]_0 = 3$ mg L^{-1}, 30 min) and over 200% upon ozonation process ($[O_3]_0 = 4$ mg L^{-1}, 5 min), prior to achieve the complete toxin degradation.

The results obtained in this work demonstrate that CWPO is particularly efficient in the simultaneous degradation of cyanobacteria and cyanotoxins compared to the conventional oxidation treatments commonly employed at DWTPs.

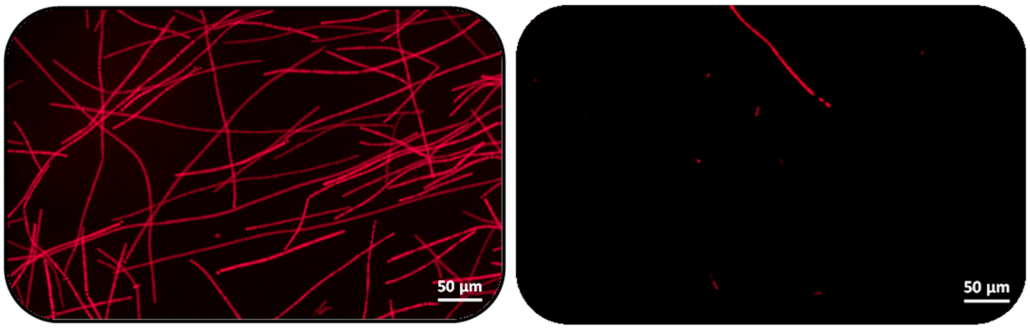

Fig. 5. Fluorescence images of Chrysosporum ovalisporum before (left) and after (right) the CWPO treatment.

3.4. Operation in real DWTP water

As a proof of concept, the potential application of the H_2O_2/Fe_3O_4-R400 catalytic system was finally evaluated using real DWTP raw (influent) and treated (effluent) waters. The real water matrixes obtained from the two DWTPs were fully characterized prior to their application. Filtered samples (0.45 µm filter) were also used to evaluate the effect of particulate matter on the CWPO performance. Table 1 shows the characterization of the real matrices corresponding to the sampling campaign of July 2021 collected from the DWTP located in Castilla y León region (see Tables S1-S5 of the Supplementary Material for all matrices characterization values).

Experiments were carried out at the same operating conditions of the experiments performed to evaluate the impact of cyanobacteria occurrence *i.e.* with a H_2O_2 concentration of 2 mg L^{-1}. Fig. 6 shows the evolution of CYN throughout the CWPO process with the real matrix characterized in Table 1 (see Fig. S6-S10 of the Supplementary Material for the experimental data obtained with all the matrices collected in the two DWTPs).

Clearly, a marked decay on the oxidation rate of CYN was observed compared to the results obtained in deionized water. The reaction rate obtained decreased following this trend: Deionized water (0.214 ± 0.01 min^{-1}) > > Filtered DWTP effluent (0.067 ± 0.0 min^{-1}) > Raw DWTP effluent (0.046 ± 0.003 min^{-1}) > Filtered DWTP influent (0.039 ± 0.006 min^{-1}) > > Raw DWTP influent (0.019 ± 0.004 min^{-1}). This trend is in good agreement with the results explained in the prior sections of this work. DWTP influent showed higher organic and inorganic dissolved carbon concentration than DWTP effluent (Table 1). As previously mentioned, the presence of bicarbonate anion in the reaction medium greatly affects the rate of toxin degradation due to its activity as hydroxyl radicals scavenger. The presence of a higher organic load also hinders the rate of toxin degradation, as it can compete with the target pollutant for the consumption of hydroxyl radicals. On the other hand, the presence of chlorides is similar for all the matrices studied. Accordingly, its effect cannot explain the differences found among them. Strikingly, the DWTP effluent showed a higher concentration of sulfate anion than the DWTP influent, another compound that act hydroxyl radicals scavenger. However, it showed less impact on these reactions than the effect observed for the presence of bicarbonates and organic matter. The differences observed between filtered and raw samples can be explained by the presence of suspended solids. Although there is a possibility that a fraction of these solids corresponds to the presence of cyanobacteria, their contribution would not be very significant due to the high efficiency of the catalytic system for their degradation as has been demonstrated in the previous section, concluding that these solids are mostly organic compounds that compete for hydroxyl radicals with the target pollutant. Finally, it seems that an increase in the conductivity of the reaction medium does not imply an adverse effect on the degradation of CYN by CWPO. Quite similar results were obtained with all the samples collected at the two DWTPs along the summer campaign, being the slight differences found among them related to the subtle composition variations of the water matrices (see Fig. S6-S10 of the Supplementary Material for the experimental data). All in all, after 90 min of CWPO reaction, almost total degradation of CYN was achieved for DWTP effluent (both, raw and filtered) and filtered DWTP influent, while raw DWTP influent experiment achieved up to 80% of CYN degradation and a process optimization was required in this case.

Table 1
Main characterization of the DWTP aqueous matrices.

	Raw DWTP influent	Filtered DWTP influent	Raw DWTP effluent	Filtered DWTP effluent
pH	7.3 ± 0.2	7.3 ± 0.2	6.8 ± 0.3	6.8 ± 0.3
TOC (mg L^{-1})	6.2 ± 0.5	6.2 ± 0.5	2.1 ± 0.3	2.1 ± 0.3
IC (mg L^{-1})	26.3 ± 0.9	26.3 ± 0.9	23.5 ± 0.5	23.5 ± 0.5
Conductivity (µS cm^{-1})	71.7 ± 1.4	71.9 ± 1.4	135.2 ± 2.1	135.1 ± 2.1
Suspended solids (mg L^{-1})	5.0 ± 0.2	0.0	2.0 ± 0.2	0.0
Cl^- (mg L^{-1})	1.5 ± 0.3	1.5 ± 0.3	1.2 ± 0.3	1.2 ± 0.3
SO_4^{2-} (mg L^{-1})	3.1 ± 0.5	3.1 ± 0.5	6.7 ± 0.2	6.7 ± 0.2

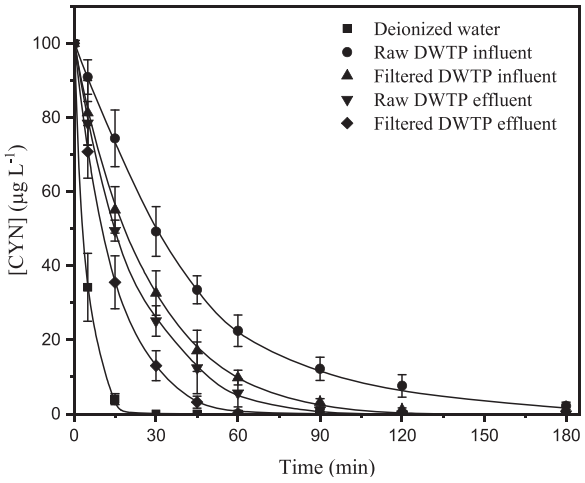

Fig. 6. Time-course of CYN concentration upon CWPO in real DWTP water ($[CYN]_0$ = 100 µg L^{-1}, $[H_2O_2]_0$ = 2 mg L^{-1}, $[Fe_3O_4$-R400] = 200 mg L^{-1}, pH_0 = 5).

In order to optimize the CWPO process, the catalyst concentration (0.2–1.0 g L^{-1}) and the oxidant concentration (2–10 mg L^{-1}) were adjusted. The most relevant results of this optimization are depicted in Fig. 7 (see Fig. S11 for all experimental data). From these results, it can be concluded that at low catalyst concentration, the limiting factor of the process is the concentration of oxidant. Total CYN degradation was achieved after 60 min by increasing the amount of H_2O_2 from 2 to 5 mg L^{-1} ($[Fe_3O_4$-R400] = 0.2 g L^{-1}), while an increment of the catalyst from 0.2 to 0.5 g L^{-1} without modifying the initial H_2O_2 concentration

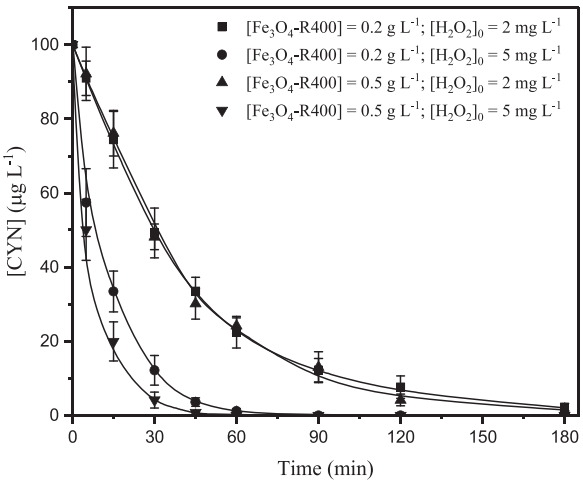

Fig. 7. Time-course of CYN concentration upon CWPO optimization in raw DWPT influent matrix ($[CYN]_0 = 100\ \mu g\ L^{-1}$, $pH_0 = 5$).

did not promote a significant increase of the degradation rate. This result is in good agreement with the previous ones, showing that the decrease in the reaction rate is mainly due to an inefficient decomposition of H_2O_2 in the presence of scavenger species. In any case, the process can be clearly optimized by adapting the H_2O_2 and catalyst concentrations to the characteristics of the influent water, showing a great versatility and providing a convincing indication that the implementation of the catalytic system should be performed as a purification step within a DWTP.

4. Conclusions

The Fe_3O_4-R400/H_2O_2 catalytic system has demonstrated to be effective for the removal of cyanotoxins in real aqueous matrices of the wide diverse characteristics that can be found in Iberian Peninsula freshwaters. The effect of several inorganic ions (SO_4^{2-}, HCO_3^-, Cl^-, $H_2PO_4^-$ and NO_3^-) and NOM in realistic concentration ranges was investigated proving that while $H_2PO_4^-$ and NO_3^- did not present significant influence on the cyanotoxin degradation rate, SO_4^{2-}, HCO_3^-, Cl^- and NOM showed a negative interference. This situation can be mainly attributed to HO· scavenging role of these compounds as well as their consumption by NOM, requiring an optimization of the operating conditions to ensure the fast removal of the cyanotoxin in the presence of high concentrations of these compounds. This process optimization can be easily performed by adapting the H_2O_2 concentration (and maybe the catalyst load as well) to the initial characteristics of the surface water, as demonstrated in real DWTP samples. Furthermore, the technology showed an outstanding performance even in the presence of cyanobacterial cells (at a relevant concentration, related to bloom occurrence), not appreciating in any case an increase of dissolved cyanotoxin concentration along the treatment. All in all, these results demonstrate the potential of the Fe_3O_4-R400/H_2O_2 catalytic system for the effective, inexpensive, eco-friendly and fast removal of cyanotoxins in drinking water treatment and open the door for further research in this field, especially addressing the scale-up of the technology.

CRediT authorship contribution statement

Conceptualization: **Samuel Cirés, Macarena Munoz, David Ortiz**; Funding acquisition: **Samuel Cirés, Zahara M. de Pedro, Frank Rogalla, Antonio Quesada, Jose A. Casas**; Investigation: **David Ortiz, José L. Arribas Mediero**; Methodology: **David Ortiz, Maria C. Crisostomo, Andrea C. Forero Ortiz, Samuel Cirés, Zahara M. de Pedro**; Project administration: **Frank Rogalla, Antonio Quesada, Jose A. Casas**; Supervision: **Macarena Munoz, Samuel Cirés, Zahara M. de Pedro, Antonio Quesada, Jose A. Casas**; Writing – original draft: **Macarena Munoz, David Ortiz**; Writing – review & editing: **Zahara M. de Pedro, Jose A. Casas**.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.110581.

References

[1] F. Garcia-Pichel, J. Belnap, S. Neuer, F. Schanz, Estimates of global cyanobacterial biomass and its distribution, Algol. Stud. 109 (1) (2003) 213–227, https://doi.org/10.1127/1864-1318/2003/0109-0213.
[2] B.A. Whitton, Ecology of cyanobacteria II: their diversity in space and time, Springer Science & Business Media, 2012, https://doi.org/10.1007/978-94-007-3855-3.
[3] P.M. Visser, J.M.H. Verspagen, G. Sandrini, L.J. Stal, H.C.P. Matthijs, T.W. Davis, H.W. Paerl, J. Huisman, How rising CO_2 and global warming may stimulate harmful cyanobacterial blooms. Harmful Algae 54 (2016) 145–159, https://doi.org/10.1016/j.hal.2015.12.006.
[4] W.W. Carmichael, The toxins of cyanobacteria, Sci. Am. 270 (1) (1994) 78–86, https://doi.org/10.1038/scientificamerican0194-78.
[5] X. He, Y. Liu, A. Conklin, J. Westrick, L.K. Weavers, D.D. Dionysiou, J.J. Lenhart, P. J. Mouser, D. Szlag, H.W. Walker, Toxic cyanobacteria and drinking water: Impacts, detection, and treatment, Harmful Algae 54 (2016) 174–193, https://doi.org/10.1016/j.hal.2016.01.001.
[6] M. Munoz, S. Cirés, Z.M. de Pedro, J.A. Colina, Y. Velásquez-Figueroa, J. Carmona-Jiménez, A. Caro-Borrero, A. Salazar, M. Santa María Fuster, D. Contreras, E. Perona, A. Quesada, J.A. Casas, Overview of toxic cyanobacteria and cyanotoxins in Ibero-American freshwaters: Challenges for risk management and opportunities for removal by advanced technologies, Sci. Total Environ. 761 (2021), 143197, https://doi.org/10.1016/j.scitotenv.2020.143197.
[7] M.G. Antoniou, A.A. De La Cruz, D.D. Dionysiou, Cyanotoxins: new generation of water contaminants, J. Environ. Engineering 131 (9) (2005) 1239–1357, https://doi.org/10.1061/(asce)0733-9372(2005)131:9(1239).
[8] P. Kumar, K. Hegde, S.K. Brar, M. Cledon, A. Kermanshahi pour, Physico-chemical treatment for the degradation of cyanotoxins with emphasis on drinking water treatment—How far have we come? J. Environ. Chem. Eng. 6 (4) (2018) 5369–5388, https://doi.org/10.1016/j.jece.2018.08.032.
[9] D. Pantelic, Z. Svircev, J. Simeunovic, M. Vidovic, I. Trajkovic, Cyanotoxins: characteristics, production and degradation routes in drinking water treatment with reference to the situation in Serbia, Chemosphere 91 (4) (2013) 421–441, https://doi.org/10.1016/j.chemosphere.2013.01.003.
[10] E. Rodríguez, G.D. Onstad, T.P.J. Kull, J.S. Metcalf, J.L. Acero, U. Von Gunten, Oxidative elimination of cyanotoxins: comparison of ozone, chlorine, chlorine dioxide and permanganate, Water Res. 41 (15) (2007) 3381–3393, https://doi.org/10.1016/j.watres.2007.03.033.
[11] D. Wang, Z. Xu, Y. Zhao, X. Yan, J. Shi, Change of genotoxicity for raw and finished water: role of purification processes, Chemosphere 83 (2011) 14–20, https://doi.org/10.1016/j.chemosphere.2011.01.039.
[12] Al Momani, F. A., & Jarrah, N, Treatment and kinetic study of cyanobacterial toxin by ozone, J. Environ. Sci. Health Part A, Toxic. /Hazard. Subst. Environ. Eng. 45 (6) (2010) 719–731, https://doi.org/10.1080/10934521003648933.

[13] G.D. Onstad, S. Strauch, J. Meriluoto, G.A. Codd, U. von Gunten, Selective oxidation of key functional groups in cyanotoxins during drinking water ozonation, Environ. Sci. Technol. 41 (12) (2007) 4397–4404, https://doi.org/10.1021/es0625327.
[14] A. Serrà, L. Philippe, F. Perreault, S. Garcia-Segura, Photocatalytic treatment of natural waters. Reality or hype? The case of cyanotoxins remediation, in: Water Research, 188, Elsevier BV, 2021, https://doi.org/10.1016/j.watres.2020.116543.
[15] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (4) (2002) 1034–1042, https://doi.org/10.1016/s0043-1354(01)00301-3.
[16] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, J. Environ. Chem. Eng. 4 (1) (2016) 762–787, https://doi.org/10.1016/j.jece.2015.12.016.
[17] J. Park, B. Yang, C. Park, J. Choi, C.M. van Genuchten, S. Lee, Oxidation of microcystin-LR by the Fenton process: kinetics, degradation intermediates, water quality and toxicity assessment, Chem. Eng. J. 309 (2017) 339–348, https://doi.org/10.1016/j.cej.2016.10.083.
[18] F.A. Al Momani, Degradation of cyanobacteria anatoxin-a by advanced oxidation processes, Sep. Purif. Technol. 57 (1) (2007) 85–93, https://doi.org/10.1016/j.seppur.2007.03.008.
[19] Y. Zhu, R. Zhu, Y. Xi, J. Zhu, G. Zhu, H. He, Strategies for enhancing the heterogeneous Fenton catalytic reactivity: a review. Applied Catalysis. B, Environmental 255 (2019), 117739, https://doi.org/10.1016/j.apcatb.2019.05.041.
[20] M. Munoz, J. Nieto-Sandoval, S. Cirés, Z.M. de Pedro, A. Quesada, J.A. Casas, Degradation of widespread cyanotoxins with high impact in drinking water (microcystins, cylindrospermopsin, anatoxin-a and saxitoxin) by CWPO, Water Res. 163 (2019), 114853, https://doi.org/10.1016/j.watres.2019.114853.
[21] M. Munoz, D. Ortiz, J. Nieto-Sandoval, S. Cirés, Z.M. de Pedro, A. Quesada, J. A. Casas, Catalytic wet peroxide oxidation of cylindrospermopsin over magnetite in a continuous fixed-bed reactor, Catalysts 10 (11) (2020) 1250, https://doi.org/10.3390/catal10111250.
[22] L.G. Devi, C. Munikrishnappa, B. Nagaraj, K.E. Rajashekhar, Effect of chloride and sulfate ions on the advanced photo Fenton and modified photo Fenton degradation process o Alizarin Red S, J. Mol. Catal. A: Chem. 374–375 (2013) 125–131, https://doi.org/10.1016/j.molcata.2013.03.023.
[23] F. Guzman-Duque, C. Pétrier, C. Pulgarin, Effects of sonochemical parameters and inorganic ions during the sonochemical degradation of crystal violet in water, Ultrason. Sonochem. 18 (1) (2011) 440–446, https://doi.org/10.1016/j.ultsonch.2010.07.019.
[24] P. Villegas-Guzman, J. Silva-Agredo, D. González-Gómez, A.L. Giraldo-Aguirre, O. Florez-Acosta, R.A. Torres-Palma, Evaluation of water matrix effects, experimental parameters, and the degradation pathway during the TiO2 photocatalytical treatment of the antibiotic dicloxacillin, J. Environ. Sci. Health, Part A 50 (1) (2014) 40–48, https://doi.org/10.1080/10934529.2015.964606.
[25] E. Lipczynska-Kochany, G. Sprah, S. Harms, Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction, Chemosphere 30 (1) (1995) 9–20, https://doi.org/10.1016/0045-6535(94)00371-Z.
[26] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (1) (2006) 1–84, https://doi.org/10.1080/10643380500326564.
[27] C. Garijo, L. Mediero, Assessment of changes in annual maximum precipitations in the Iberian Peninsula under climate change, Water 11 (11) (2019) 2375, https://doi.org/10.3390/w11112375.
[28] S. Álvarez-Torrellas, M. Munoz, V. Mondejar, Z.M. de Pedro, J.A. Casas, Boosting the catalytic activity of natural magnetite for wet peroxide oxidation, Environ. Sci. Pollut. Res. 27 (2020) 1176–1185, https://doi.org/10.1007/s11356-018-2171-3.
[29] Confederación Hidrográfica del Tajo (2022). Aguas Superficiales: Control fisicoquímico. ⟨http://www.chtajo.es/LaCuenca/CalidadAgua/Resultados_Informes/Paginas/RISupFisicoQu%C3%ADmico.aspx⟩.
[30] Confederación Hidrográfica del Ebro. (2022). Resultados analíticos. ⟨https://www.chebro.es/web/guest/resultados-anal%C3%ADticos⟩.
[31] Confederación Hidrográfica del Guadiana. (2022). *Datos analíticos por punto de control.* ⟨https://www.chguadiana.es/cuenca-hidrografica/calidad-y-estado-de-las-masas-de-agua/aguas-superficiales/datos-analiticos-por-punto-de-control/datos-analiticos⟩.
[32] A.A. de la Cruz, A. Hiskia, T. Kaloudis, N. Chernoff, D. Hill, M.G. Antoniou, X. He, K. Loftin, K. O'Shea, C. Zhao, M. Pelaez, C. Han, T.J. Lynch, D.D. Dionysiou, A review on cylindrospermopsin: the global occurrence, detection, toxicity and degradation of a potent cyanotoxin, Environ. Sci.: Process. Impacts 15 (11) (2013), https://doi.org/10.1039/c3em00353a.
[33] M. Lu, Y. Chang, I. Chen, Y. Huang, Effect of chloride ions on the oxidation of aniline by Fenton's reagent, J. Environ. Manag. 75 (2) (2005) 177–182, https://doi.org/10.1016/j.jenvman.2004.12.003.
[34] S. Merel, M. Clément, A. Mourot, V. Fessard, O. Thomas, Characterization of cylindrospermopsin chlorination, Sci. Total Environ. 408 (2010) 3433–3442, https://doi.org/10.1016/j.scitotenv.2010.04.033.
[35] E.M. Siedlecka, A. Więckowska, P. Stepnowski, Influence of inorganic ions on MTBE degradation by Fenton's reagent, J. Hazard. Mater. 147 (1) (2007) 497–502, https://doi.org/10.1016/j.jhazmat.2007.01.044.
[36] F.J. Beltrán, G. Ovejero, J. Rivas, Oxidation of polynuclear aromatic hydrocarbons in water. 4, Ozone Comb. Hydrog. peroxide. *Ind. Eng. Chem. Res.* 35 (3) (1996) 891–898, https://doi.org/10.1021/ie9503757.
[37] E. Illés, A. Mizrahi, V. Marks, D. Meyerstein, Carbonate-radical-anions, and not hydroxyl radicals, are the products of the Fenton reaction in neutral solutions containing bicarbonate, Free Radic. Biol. Med. 131 (2019) 1–6, https://doi.org/10.1016/j.freeradbiomed.2018.11.015.
[38] Mingyu, L., Kunkun, W., Yilin, T., Gang, R. & Lin, S. (2011). Effect of inorganic ions on Fenton's reagent catalytic degradation of phenol in water. 2011 International Conference on Computer Distributed Control and Intelligent Environmental Monitoring, 11140–1147. 10.1109/CDCIEM.2011.501.
[39] J.E. Grebel, J.J. Pignatello, W.A. Mitch, Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters, Environ. Sci. Technol. 44 (17) (2010) 6822–6828, https://doi.org/10.1021/es1010225.
[40] A. De la Rubia, M. Rodriguez, D. Prats, pH, Ionic strength and flow velocity effects on the NOM filtration with TiO_2/ZrO_2 membranes, Sep. Purif. Technol. 52 (2) (2006) 325–331, https://doi.org/10.1016/j.seppur.2006.05.007.
[41] F. Wang, Y. Wu, Y. Gao, H. Li, Z. Chen, Effect of humic acid, oxalate and phosphate on Fenton-like oxidation of microcystin-LR by nanoscale zero-valent iron, Sep. Purif. Technol. 170 (2016) 337–343, https://doi.org/10.1016/j.seppur.2016.06.046.
[42] G. Grützmacher, G. Böttcher, I. Chorus, H. Bartel, Removal of microcystins by slow sand filtration, Environ. Toxicol. 17 (4) (2002) 386–394, https://doi.org/10.1002/tox.10062.
[43] J.A. Westrick, D.C. Szlag, B.J. Southwell, J. Sinclair, A review of cyanobacteria and cyanotoxins removal/inactivation in drinking water treatment, Anal. Bioanal. Chem. 397 (5) (2010) 1705–1714, https://doi.org/10.1007/s00216-010-3709-5.
[44] Real Decreto 3/2023, de 10 de enero, por el que se establecen los criterios técnico-sanitarios de la calidad del agua de consumo, su control y suministro. Boletín Oficial del Estado, 9, de 11 de enero de 2023. ⟨https://www.boe.es/eli/es/rd/2023/01/10/3⟩.
[45] S. Cirés, A. Ballot, A review of the phylogeny, ecology and toxin production of bloom-forming Aphanizomenon spp. and related species within the Nostocales (cyanobacteria), Harmful Algae 54 (2016) 21–43, https://doi.org/10.1016/j.hal.2015.09.007.
[46] J. Fan, L. Ho, P. Hobson, R. Daly, J. Brookes, Application of various oxidants for cyanobacteria control and cyanotoxin removal in wastewater treatment, J. Environ. Eng. 140 (7) (2014), 04014022, https://doi.org/10.1061/(ASCE)EE.1943-7870.0000852.
[47] X. Li, W. Song, S. Chen, Kinetics and mechanism of ozonation to treat Microcystis-laden source waters affected by cell-viability, J. Hazard. Mater. 439 (2022), 129604, https://doi.org/10.1016/j.jhazmat.2022.129604.stylefix.