Chemical Engineering Journal Advances 11 (2022) 100318

Contents lists available at ScienceDirect

Chemical Engineering Journal Advances

journal homepage: www.sciencedirect.com/journal/chemical-engineering-journal-advances

Calcium peroxide (CaO_2) granules enclosed in fabrics as an alternative H_2O_2 delivery system to combat Microcystis sp.☆

Eleni Keliri [a], Panayiota Adamou [a], Nektarios Efstathiou [a], Despoina Kokkinidou [b], Konstantinos Kapnisis [b], Andreas S. Anayiotos [b], Hanna Mazur-Marzec [c], Maria G. Antoniou [a,*]

[a] Department of Chemical Engineering, Cyprus University of Technology, 3036, Limassol, Cyprus
[b] Department of Mechanical Engineering and Materials Science and Engineering, Cyprus University of Technology, 3036, Limassol, Cyprus
[c] Division of Marine Biotechnology, Faculty of Oceanography, University of Gdańsk, M. J. Piłsudskiego 46, PL-81378 Gdynia, Poland

ARTICLE INFO

Keywords:
Calcium peroxide
Microcystis sp.
Oxidation
Fabrics
Treatment

ABSTRACT

Hydrogen peroxide (H_2O_2) is considered the most environmentally friendly method to combat toxic cyanobacterial as it selectively oxidizes them without forming harmful by-products. Recently, calcium peroxide (CaO_2) granules were proposed as an alternative algaecide to liquid H_2O_2 for their slow H_2O_2 release properties. Herein, concentrations of 0.5, 1.0, and 2.0 g/L CaO_2 granules were added into a surface water matrix to investigate their H_2O_2 releasing properties. Then, select concentrations of granules were enclosed in four types of fabric delivery systems to evaluate their overall oxidant releasing capacity. No difference was observed between the maximum H_2O_2 concentrations of the direct application of granules and the fabric delivery systems for types A – C, which released up to 12 mg/L H_2O_2 by 2.0 g/L CaO_2 granules at $t = 24$ h. Fabric system type D had the lowest H_2O_2 releasing capacity. Based on the above, delivery systems A to C were further investigated for their suitability to combat cyanobacteria. To examine their efficiency on *Microcystis* sp., bench-scale treatments were performed in various CaO_2 granules enclosed in fabrics (GEF) concentrations. GEF type B of concentration 2 g/L and type C concentrations of 1 g/L and 2 g/L were sufficient to reduce the photosynthetic activity of *Microcystis* species from 8000 to <1000 RFU. GEFs can be considered as a sustainable method to combat cyanobacterial blooming, since they minimize granules' availability into the waterbody, and hence eliminate adverse impact on non-targeted species. Moreover, these delivery systems promote the circular economy by implementing practices that make use of reused and recycled fabrics.

1. Introduction

Surface water contamination events caused by high nutrient and organic matter loads lead to the overgrowth of some phytoplankton species known as cyanobacteria. In such eutrophication events, these phototrophic bacteria are blooming giving a characteristic cyano-colour to the water, as well as distinct odour and taste [1]. Besides the aesthetic effects, cyanobacterial blooming causes oxygen depletion, stratification, disruption of the aquatic life balance, as well as light inhibition that limits phytoplankton's ability to photosynthesize. Moreover, cyanobacteria can excrete toxins (cyanotoxins) and other secondary metabolites with harmful effects to aquatic life. Reports on toxic cyanobacteria blooms in waterbodies are exponentially increasing the past years, making it a major environmental issue of concern that urgently needs to be addressed [2]. *Microcystis* sp., a genus of freshwater cyanobacteria with a single-cell morphology that tend to form colonies embedded to a matrix, is the most detected cyanobacterium in freshwater. Blooms of *Microcystis* are gradually becoming more prevalent and persistent, posing a direct threat to aquatic ecosystems and mammalian health due to their ability to excrete cyanotoxins into the water [3–5]. The most known are the Microcystins (MC) with the most detected analogues to be the MC-LR, MC-RR, and MC-YR. Moreover, their presence in surface waters of high ecological importance increase the demand for efficient, cost-effective, and environmentally responsible solutions for their *in-situ*

Abbreviations: GEF, Granules Enclosed in Fabrics; TDS, Total Dissolved Solids; TP, Total Phosphorous; TN, Total Nitrogen; SD, Standard Deviation; PSII, Photosystem II; MDL, Method Detection Limit; Ft, Fluorescence; QY, Quantum Yield; SEM, Scanning Electron Microscope.

☆ Resubmitted to the *Chemical Engineering Journal Advances April 2022*

* Corresponding author.
E-mail address: maria.antoniou@cut.ac.cy (M.G. Antoniou).

https://doi.org/10.1016/j.ceja.2022.100318
Received 31 December 2021; Received in revised form 29 April 2022; Accepted 3 May 2022
Available online 4 May 2022

mitigation.

Several methods have been applied over the years to treat cyanobacterial blooms, that exhibited various efficiencies [6,7]. The past decade, a chemical method utilizing liquid hydrogen peroxide (H_2O_2) was explored as an alternative to copper algicides and a more environmentally friendly treatment solution [8,9]. H_2O_2 decomposes into oxygen and water, while when it is applied in the presence of a catalyst it can form reactive oxygen species (ROS) with high oxidative potential (Eq.1; Eq.2). Treatment with H_2O_2 proved to be efficient for several occasions and blooming events as it selectively suppresses cyanobacteria by inhibiting their photosynthetic activity [10,11]. However, blooms of *Microcystis* sp. that were more persistent required high H_2O_2 doses (> 7 mg/L) during treatment, doses that found to cause mobility issues to the zooplankton community when are applied directly [12]. A study by Wang et al. [13] showed that repeated additions of liquid H_2O_2 extent the residual effect of the oxidant into the water column, while resulting in successful *Microcystis* sp. mitigation [13]. This application method enhances the prospects of H_2O_2 *in-situ* application since it avoids overdosing and the undesirable side-effects of high single doses.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (1)$$

$$H_2O_2 + catalyst \rightarrow OH^- + HO^{\cdot} \quad (2)$$

Calcium peroxide (CaO_2) granules have been applied on a broad spectrum of environmental remediation processes over the last few years due to their potency to slowly release H_2O_2 and oxygen through a parallel reaction system Eqs.3, 4 and (5). Kinetic studies on their reaction pathways showed that once granules are applied into the water, they can directly react with water to form H_2O_2 and oxygen without the presence of a catalyst [14]. CaO_2 granules were tested for soil and groundwater remediation, as well as for odour control, chemical decomposition, and oxidation of persistent contaminants [15].

$$CaO_2 + 2H_2O \rightarrow Ca(OH)_2\downarrow + H_2O_2 \quad (3)$$

$$CaO_2 + 2H_2O \rightarrow Ca^{2+} + 2H_2O_2 \rightarrow Ca^{2+} + 2OH^- + 2HO^{\cdot} \rightarrow Ca(OH)_2\downarrow + 2HO^{\cdot} \quad (4)$$

$$CaO_2 + H_2O \rightarrow Ca(OH)_2\downarrow + \frac{1}{2}O_2 \quad (5)$$

Their application for restoring surface waters could be useful when multiple liquid H_2O_2 doses are required, since granules continuously release H_2O_2 into a water matrix. Other important characteristics of CaO_2 granules are their (a) orthorhombic structure which provides high thermal stability against its decomposition, (b) low solubility (almost insoluble) in water, and (c) inexpensive production line which requires only low-cost raw materials. There are a few studies on the application of CaO_2 granules for treating cyanobacteria contaminated surface water, especially for controlling *Microcystis* blooms [16–18]. The most recent study reported a gradual and controlled release of H_2O_2 that outperformed liquid H_2O_2 when applied in a naturally occurred *Merismopedia* sp. bloom [19]. Also, other types of granules and beads containing CaO_2 were fabricated and used for the mitigation of cyanobacteria resulting in high treatment efficiency [20,21]. These studies outline the potential of this compound to be used in an array of applications due to its physical, chemical, and cyanocidal properties.

Nevertheless, attention should be given on the environmental impact of granules when they are applied directly into a contaminated waterbody. These granules tend to also release calcium hydroxide as a precipitate (eq.3–5) that significantly increases the solution pH [22]. In cases of cyanobacterial contamination, the pH of the aquatic medium is already elevated (pH = 8 – 10), which means that further increase will cause additional distress to the aquatic environment [23,24]. Also, the size and shape of granules make them available for consumption by fish and other aquatic species when they are applied directly, which is deemed to be dangerous for their wellbeing. Another concern for their *in-situ* application is their accumulation in soil which may disrupt its chemistry and affect other bacteria and zooplankton existing there [25]. Lastly, since oxygen is released with their dissolution, they can flocculate on the surface, which means that specialized and costly equipment is needed for their collection and disposal after the treatment. Therefore, it is essential to eliminate their potential side effects stated above in order to safeguard not only water quality but the entire aquatic ecosystem. Hence, CaO_2 granules availability into a waterbody should be minimized when they are applied to treat cyanobacteria contaminated sites.

In this study, CaO_2 granules were enclosed in four types of fabrics: (A) pocket lining, (B) interlining textile, (C) polyester netting, and (D) paper filter wrapped in tights; to examine their H_2O_2 releasing capacity compared with their direct application into a surface water. We hypothesized that by enclosing the granules into a textile material will allow them to keep their initial H_2O_2 releasing properties but act in a more controlled manner, minimizing their undesirable side effects. Then, granules enclosed in fabrics (GEF) were applied into surface water spiked with pure *Microcystis* culture, to test their efficiency on mitigating a dense and resistant bloom. The above investigations allowed to conclude if GEF delivery systems can potentially be applied *in-situ* to combat cyanobacterial blooming. The outcomes of these investigations will provide a proof whether GEF systems can be a vital alternative, and a more environmentally friendly approach since they minimize granules' availability into the water column. In addition, the application of GEF systems is aligned with the UN SDG goals of circular economy as reused and recycled fabrics can be used for treatment purposes.

2. Materials & methods

2.1. Surface water sampling and analysis

Surface water was collected from Kouris dam located in Limassol, Cyprus. Sampling was performed at an accessible point of the dam and water was collected from 0.1 to 0.2 m below the surface with the use of a bucket. Samples were collected in acid-washed polyethylene (PE) bottles and brought to the laboratory for analysis and matrix preparation. To ensure consistency in the experimental conditions, samples were taken from each water collection event and physicochemical water characterization was performed. Parameters such as pH, conductivity, salinity, total dissolved solids (TDS) were measured using the ExStik®-portable probe (EXTECH, FLIR Systems), while total nitrogen (TN) and total phosphorus (TP) concentration was determined by using Spectroquant® cell test kits (Merck Millipore) equivalent to EPA and APHA standard analytical methods; and the Spectroquant® Pharo 300 spectrophotometer (Merck). The method detection limit (MDL) and method standard deviations (SD) were 0.50 mg-N/L, 0.05 mg-P/L, and 0.15 mg-N/L, 0.027 mg-P/L, respectively. Initial instantaneous fluorescence (Ft) and quantum yield (QY) of the Photosystem II (PSII) of collected samples were measured by AquaPen AP 110/C (Photon Systems Instruments, Czech Republic) equipped with blue ($\lambda = 450$ nm) and red ($\lambda = 620$ nm) LED light emitters for chlorophyll-a and phycocyanin fluorescence, respectively. The maximum quantum yield of the PSII was recorded as a fraction of the maximal variable fluorescence (Fv = Fm-Fo) to the maximal fluorescence intensity in the dark-adapted state (Fm).

2.2. CaO_2 granules and GEF system characterization

CaO_2 granules were utilized in this study to determine their H_2O_2 release properties in surface water matrix in two cases: (a) when they are directly applied, and (b) when they are enclosed in a textile material. CaO_2 granules were provided in the form of "IXPER® 70CG" product by Solvay Chimika S.A. (free samples). Their purity was 70% w/w CaO_2, which is equivalent to ~15.5% available oxygen, and particle size of 0.5 – 2 mm. Impurities reported by the manufacturer were $Ca(OH)_2$ of 10–19% and other inorganic calcium compounds of around 5–19%. XRF

analysis was performed by portable, handheld XRF elemental analyser (ProSpector 3, Elvatech) to determine the elemental composition of CaO_2 granules.

Four types of fabrics were utilized in this study: "type A = natural twill fabric for pocket lining", "type B = non-woven interlining fabric (fusing paper)", "type C = polyester mosquito netting fabric", and "type D = paper filter wrapped in 20 DEN tights", as shown in Fig. 1.

QUANTA 400F Field Emission high-resolution scanning electron microscope (SEM) was used to examine the surfaces of woven and non-woven fabric samples at an acceleration voltage of 10 kV. The textile samples were coated with 10 nm Au/Pd prior to SEM observation.

SEM - FEI Quanta 200 (Oregon, USA) scanning electron microscope with a Secondary Electrons Detector was used to evaluate the properties of the fabrics (pore area, size, and thickness). Prior to SEM observation, fabrics were deposited onto carbon tapes, which were mounted on aluminium stubs. A cross-sectional multipurpose specimen holder was also used to measure the thickness of the fabrics. Obtained SEM images were processed and analysed with the use of "ImageJ" public domain software to determine the porous area of each material [26]. The pore area of each material was measured by determining the average surface area of 60 pores (20 pores in each image x 3).

2.3. H_2O_2 release kinetics

Experiments on the release of H_2O_2 by CaO_2 granules were performed in 250 mL glass containers. Initially, concentrations of 0.5, 1.0, and 2.0 g/L CaO_2 granules were directly added into a vessel contained 200 mL of surface water collected from Kouris Dam (Limassol, Cyprus) to capture their H_2O_2 release kinetics. Same quantities were then placed and folded in fabric materials of types A to D and nylon cables were tied at the two ends to enclose the system (Scheme S1). Each fabric was cut into pieces of 5 × 5, 6 × 6, and 7 × 7 inches, to enclose 0.5, 1.0, and 2.0 g/L of CaO_2 granules, respectively. As a control, a medium sized fabric piece was folded without the addition of granules. Each fabric encapsulating the CaO_2 granules dose was added into a glass container with 200 mL of surface water from Kouris dam (Scheme S2).

To monitor the instantaneous concentration of H_2O_2, 2 mL of sample was collected from each flask at t = 0, 1, 2, 4, 6, 24, 48 h and was analysed with a colorimetric method introduced by Sellers et al. [27]. In brief, 2 mL of sample was filtered through a PVDF syringe filter (0.22 μm) and immediately reacted with 0.2 mL of titanium oxalate oxide (C = 50 g/L) and 0.2 mL sulfuric acid (1 + 17 v/v), both reagents purchased from Sigma – Aldrich. The absorbence at λ = 400 nm was measured by the TECAN Infinite 200 spectrophotometer in a 96-well plate. The concentration of H_2O_2 was quantified based on a calibration curve that ranged between 0.5 and 20 mg/L H_2O_2. In addition, the physicochemical characteristics of the treated solutions were recorded at t = 0, and 24, and 48 h including pH, conductivity, TDS, and salinity (ExStick probe-EXTECH).

All the experiments were performed in triplicates and conducted under the same laboratory conditions, in a set temperature of 20 °C, and a continuous light of 800 (± 200) Lux.

2.4. *Microcystis* cultivation and cyanotoxins concentration

Pure *Microcystis* sp. culture cultivated in a BG-11 medium at the Water Treatment Laboratory-AQUA of the Cyprus University of Technology, was utilized to spike cyanobacteria cells in surface water for bench-scale treatment experiments. The cultivated *Microcystis* cultures were filtered through cellulose nitrate membrane filter (0.45 um) and the pure cells were collected into a petri dish with the use of a sterile plastic scrubber to scrub them from the filter surface. Cyanobacteria cells were then gradually added into surface water until Ft reached 8000 RFU to simulate a blooming event.

To examine the toxicity of the cultivated cultures, 5 mL (x3) of *Microcystis* sp. (FT = 16,000) passed through GF/C filter (0.45 μm) and samples were extracted in 2 mL of 75% methanol in water by homogenizing the filter containing cyanobacteria cells with a glass rod. Then, samples were sonicated for 10 min, vortexed for 5 min and centrifuged at 14,000 rpm for 10 min. The supernatant was transferred to a chromatographic vial and analysed with LC-MS/MS system. Chromatographic separation of sample components was performed on Zorbax Eclipse XDB-C18 column (4.6 mm ID (inner diameter) × 150 mm, 5 μm; Agilent Technologies, Santa Clara, CA, USA) by gradient elution with a mixture of 5% acetonitrile in Milli-Q water (solvent A) and acetonitrile (solvent B), both containing 0.1% formic acid. The system was composed of an Agilent 1200 (Agilent Technologies, Waldboronn, Germany) chromatograph coupled online to a hybrid triple quadrupole/linear ion trap mass spectrometer (QTRAP5500, Applied Biosystems, Sciex, Concord, ON, Canada). Mass spectrometer with a turbo ion source (550 °C, 5.5 kV) operated in positive mode [28]. Standards of microcystins used in the analysis were from Alexis Biochemicals and the detection limit for used standards was 0.1 ng/mL. For data acquisition and processing Analyst® Software (version 1.5.1, Applied Biosystems, Concord, ON, Canada) was used.

2.5. *Treatment of Microcystis sp*

To examine the feasibility of applying CaO_2 granules enclosed in fabrics for the mitigation of *Microcystis* sp. in surface waters, fabric delivery systems of types A to C were utilized to encapsulate the granules, as described previously. For the matrix preparation, the collected *Microcystis* mass was spiked into the surface water, slightly enriched with BG-11 medium (1% v/v), and the Ft at λ = 620 nm was monitored with the AquaPen AP 110/C (Photon Systems Instruments, Czech Republic). Mass was gradually added into the surface water until the Ft value reached 8000 RFU. The prepared matrix was stored in PE bottle with an open lid for 12–18 h to acclimatize, at T = 20 °C, and a continuous light source of 800 (± 200) Lux.

Quantities of 0.0, 0.5, 1.0, and 2.0 g/L CaO_2 granules were enclosed in fabrics type A, B and C, and added in 200 mL of the prepared contaminated matrix. Ft and QY values at λ = 620 nm were recorded at t = 0, 6, 24, 48 h utilizing AquaPen AP 110/C in order to monitor the destruction of cyanobacterial cells and photosystem II (PSII) inactivation, thus evaluating the efficiency of the enclosed granular oxidant on mitigating *Microcystis* sp..

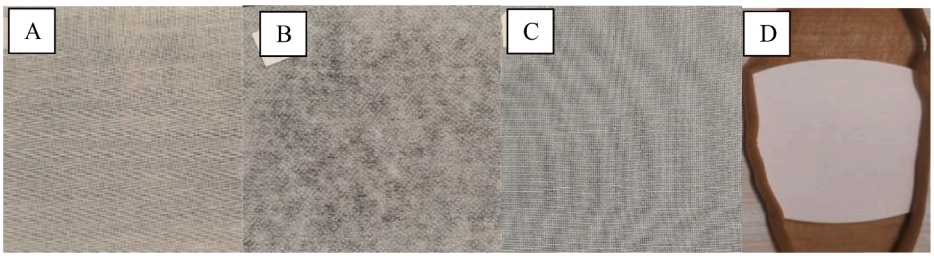

Fig. 1. Fabrics utilized to enclose CaO_2 granules: (A) natural twill fabric for pocket lining, (B) non-woven interlining fabric (fusing paper), (C) polyester mosquito netting fabric, and (D) paper filter wrapped in 20 DEN tights.

Physicochemical characteristics such as pH, conductivity, TDS, and salinity were measured at $t = 0$, 24, and 48 h, with the use of ExStick probe (EXTECH). Instant H_2O_2 concentration during treatment was monitored by the colorimetric method mentioned before. All the experiments were performed in triplicates and conducted under the same laboratory conditions, in a set temperature of 20 °C, and a continuous light of 800 (± 200) Lux.

2.6. Statistical analyses

Data processing and statistical analysis were performed with the use of PRISM®-GraphPad software, version 9.3.1. Each experiment was performed in triplicates and for each measured parameter, the mean and standard deviation (SD) values were calculated. Data are presented on graphs as the mean with SD error bar and/or on tables as mean ± SD. When comparing the H_2O_2 release curves and the treatment efficiencies, one-way ANOVA followed by a Turkey's test were performed.

3. Results

3.1. Water matrix composition

Nutrient concentrations were stable during the sampling period and found to be below the MDL (TN < 0.5 mg/L; TP < 0.05 mg/L;). The eutrophic status of the waterbody based on its nutrient content is characterized as oligotrophic in all the collected samples. Other physicochemical characteristics such as pH, total dissolved solids, salinity, and conductivity were 8.5 ± 0.3, 440 ± 30 (mg/L), 310 ± 20 (ppm), and 620 ± 30 (μS/cm), respectively. The measured Ft and QY at $\lambda_{excitation} = 620$ nm were to the lower detection limit of the instrument (50 RFU, QY = 0.2), meaning that there was no any extensive activity and productivity of cyanobacteria into the water. Thus, surface water used in the experiments was partially free from cyanobacteria and other phytoplankton species were at low levels. Once the water was spiked with pure *Microcystis* culture, a significant FT measurement was recorded (Ft = 8000). Surface water spiked with pure *Microcystis* sp. resulted in a mono-dominated artificial bloom which was utilized to examine the treatment efficiency of GEF systems. After spiking surface water with cyanobacteria, the physicochemical water characteristics were measured to ensure maintenance of the initial conditions (Table 1). *Microcystis* scum that was collected on GF/C filters, extracted in methanol, and analysed with LC-MS/MS for its intracellular cyanotoxin content, confirmed the presence of intracellular MC-RR and MC-YR in concentrations of 4.66 μg/L and 1.45 μg/L, respectively.

3.2. CaO_2 granules and fabrics characterization

CaO_2 granules were analysed for their elemental composition regarding as presented in Table S1. The main elements comprising granules were calcium and oxygen (light elements), however some heavy metals like iron, nickel, and manganese were detected in the granular material based on the XRF analysis.

SEM was performed to characterize the morphology, pore area, and thickness of the four-textile materials utilized to enclose the granules. As shown in Fig. 1, SEM images showed fabrics of different material characteristics in regards with their morphology, pore shape and fibre networks' structure. The total surface area covered in each SEM image was measured with ImageJ software and found to be 7.7 ± 0.1 mm^2. It can be observed from Fig. 2(A) that fabric type A surface is smooth and clean, displaying a well-structured twilled fabric. The pores are distributed almost evenly in the surface of the fabric, resulting in a typically hierarchical pore network structure composed of cotton and polyester fibres. Fig. 2(B) depicts the interlining fabric, with areas that are thermally compressed to shape visible dots on the fusing paper. Those spots have zero porosity and cover around 18% of its surface area. The fibres were not structurally distributed in the non-woven fabric and therefore pores are being shaped by the available spaces between the tangled fibres. Fabric type C depicted in Fig. 2(C), had the most strict and repeatable structure with rectangle spaces between the twilled fabric that shape its pores. Parallel horizontal lines of fabric bundles are observed with vertically braided fabrics that are shaping knots to keep its fabric network. Fig. 2(D) shows the 20 DEN tights comprised by knitted nylon fibre networks with nodes that allow the formation of pores between the intersected fabric lines.

The regular pore area (mm^2) of each material was defined with the use of "ImageJ" software by measuring the surface area of 60 pores for each fabric and then calculating the average pore size, the standard deviation as well as identifying the minimum and maximum pore size to determine a surface area range (Table 2). For Fabric type C, pore radius and dimeter are not available (N/A) since the shape of the pores were selected to be rectangular instead of circular, as it fitted better the pore shape. The total coverage of pores on the surface of each material was calculated and found to be 5.7%, 19%, 12% for fabric type A, C, and D, respectively (Scheme S3).

3.3. H_2O_2 release by CaO_2 granules

3.3.1. H_2O_2 release kinetics

Bench-scale experiments were conducted to evaluate the H_2O_2 yield by CaO_2 granules when they are directly applied into a surface water matrix, and when a delivery system is used. CaO_2 granules direct application into a surface water (Kouris dam) resulted in a rapid H_2O_2 release within the first 6 h. The ability of granules to release H_2O_2 continued for up to 24 h where the maximum accumulative concentration reached a plateau. A linear and a non-linear regression analysis was performed to further investigate the kinetics. The release curves fitted well to the one-phase association model, as shown in Fig. 3, which describes a pseudo-first order kinetic model, giving better correlation coefficients than the non-linear correlation fit (Figure S1). This means that the initial dose of CaO_2 granules affects their H_2O_2 releasing properties, hence it verifies that the release cannot follow a zero-order kinetic curve as it has been previously reported in the literature. The simulative parameters of the one-phase association model fitting the equation: $Y = Y0 + (Plateau-Y0) * (1-exp(-K*x))$, are presented in Table 3.

Calcium peroxide granules enclosed in fabrics resulted in a continuous release similar to their direct application, following again a pseudo-first order association kinetics model. Correlation coefficients derived from pseudo-zero-order model were much lower than the ones from the one-phase association analysis (Figure S2). Calculated correlation coefficients ranged between 0.62 and 0.99, as shown on Fig. 4, displaying a sufficient correlation fit to the model for GEF types A, B and C. Those exhibited similar accumulative H_2O_2 released concentrations compared with the ones released by the direct application of CaO_2

Table 1
Physicochemical characteristics of the aqueous matrix comprising of surface water (Kouris dam) spiked with 1% BG-11 and pure *Microcystis* culture. Initial water parameters, treatment experiment at $t = 0$ h.

	pH	Conductivity	S	TDS	Ft	QY	TN	TP	MC_RR	MC_YR
units	–	μS/cm	ppm	mg/L	RFU	–	mg/L	mg/L	μg/L	μg/L
Value	9.5	650	300	430	8000	0.45	3.0	0.50	4.66	1.45
(±SD)	0.5	40	40	60	700	0.05	0.3	0.15	–	–

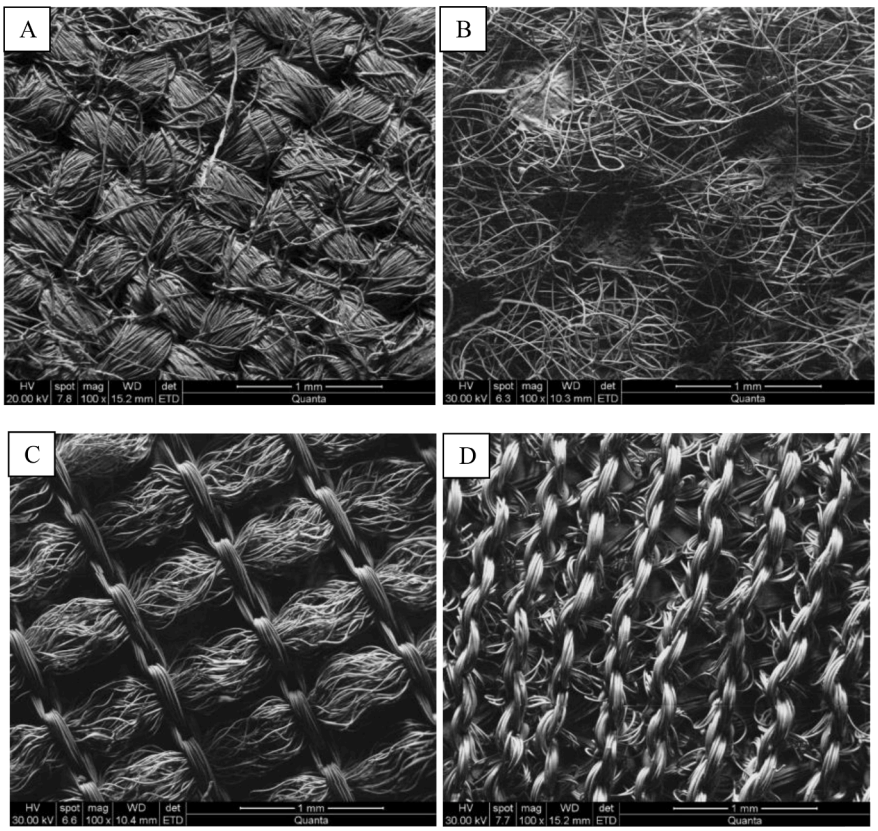

Fig. 2. SEM images of fabric types A – D, with a magnification of 100x at a set scale of 1 mm.

Table 2
Pore size range of fabrics Type A–C, mean pore size ± SD (um), $n = 60$ pores.

Fabric	Average poresurface area	±SD	Min	Max	R	D	Thickness
units	mm^2				Mm		μm
A	0.016	0.006	0.007	0.033	0.07	0.14	260
B	0.004	0.003	0.001	0.020	0.04	0.08	200
C	0.113	0.022	0.072	0.157	N/A	N/A	170
D	0.009	0.005	0.003	0.024	0.5	0.1	554

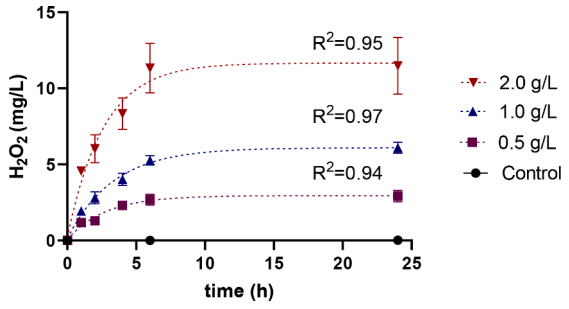

Fig. 3. H_2O_2 release kinetics by 0.5, 1.0, 2.0 g/L CaO_2 granules in surface water (Kouris dam), fitted by non-linear pseudo-first order model: $Y = Y0 + (Plateau-Y0)*(1-exp(-K*x))$.

granules. GEF type D was the only system that released significantly lower H_2O_2 concentrations than the other GEF types ($p < 0.05$), which indicates a high inhibiting effect of H_2O_2 to diffuse from the filter to the bulk of the solution or its reaction with the filter itself. For GEF type D, the highest tested concentration of 2 g/L resulted in a maximum release of just 1.2 ± 0.9 mg/L H_2O_2 at $t = 24$ h, while GEF systems of type A, B and C released up to 11.9 ± 0.4 mg/L H_2O_2, 13.5 ± 1.2 mg/L H_2O_2, and 12.0 ± 0.5 mg/L H_2O_2, respectively (Fig. 4, Table S2).

3.3.2. H_2O_2 yield and dose correlation

Direct application of granules into the water matrix as well as the GEF systems exhibited a linear relationship between the released H_2O_2 concentration and the added CaO_2 granules dose ($R^2 = 0.97–0.98$). This means that the H_2O_2 yield per CaO_2 weight unit applied in water remains constant. The use of fabrics A to C as delivery systems did not affect this linear relationship between applied CaO_2 dose and H_2O_2 yield (Fig. 5). Specifically, 0.5, 1.0, and 2.0 g/L CaO_2 granules released around 3.0 mg/L H_2O_2, 6.0 mg/L H_2O_2, and 12.0 mg/L H_2O_2, respectively. Those yields were obtained by all tested fabrics except type D that gave a significantly lower R^2 value, which was anticipated based on its minimal H_2O_2 releasing potential (Table S2, Figure S3).

3.4. GEF application for Microcystis sp. mitigation

3.4.1. Treatment efficiency (Ft, QY)

Following the completion of the release H_2O_2 experiments, the effectiveness of the proposed H_2O_2 delivery systems (types A-C) on the treatment of a *Microcystis* sp. bloom was investigated. Each system was evaluated by recording the phycocyanin instantaneous fluorescence (Ft) and quantum yield (QY) of the photosystem II at $\lambda = 620$ nm throughout

Table 3
Simulative parameters of the one-phase association model fitting the equation: $Y = Y0 + (Plateau-Y0)*(1-exp(-K*x))$ for the H_2O_2 release curves obtained by 0, 0.5, 1.0, and 2.0 g/L CaO_2 granules, and 2.0 g/L CaO2 granules enclosed in Fabric type A, B, C, and D..

Best-fit values	Control	0.5	1.0	2.0	A	B	C	D
Y0	−0.00	0.063	0.127	0.185	−0.01	−0.02	−0.67	−0.09
Plateau	Unstable	2.950	6.094	11.66	10.99	13.66	12.38	1.607
K	0.000	0.360	0.299	0.378	0.693	0.409	0.248	0.061
Span	Unstable	2.887	5.967	11.48	11.00	13.69	13.06	1.693

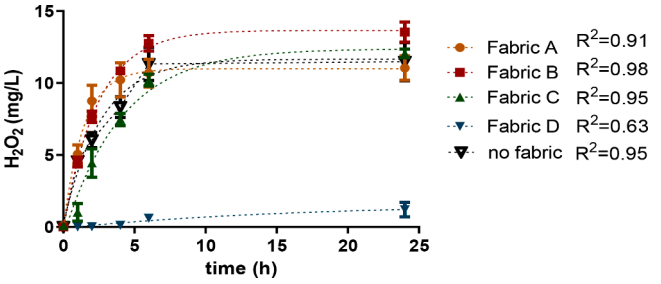

Fig. 4. H_2O_2 release kinetics by 2.0 g/L CaO_2 GEF types A – D, and no fabric, in a surface water (Kouris dam) fitted by non-linear pseudo-first order model: $Y = Y0 + (Plateau-Y0)*(1-exp(-K*x))$.

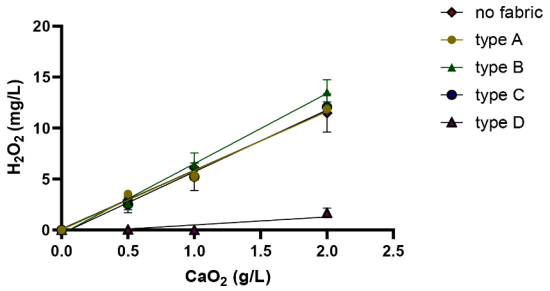

Fig. 5. Linear correlation between H_2O_2 yield at $t = 24$ h and CaO_2 granules' dose directly applied (no fabric) and applied enclosed in GEF types A – D.

treatment. The experimental conditions in all investigations were the same, with the initial fluorescence and QY to be at 8000 ± 700 RFU, and 0.45 ± 0.05, respectively. The obtained results are summarized in Figs. 6 and 7. Starting from the highest enclosed dose of 2.0 g/L in GEF types B and C a significant reduction of Ft (87.5 – 91%, $t = 48$ h) was observed. This reduction was also reflected in the respective quantum yields, where a significant decrease was recorded (77.8 – 82.5%) for 2.0 g/L GEF type B and C, as shown in Fig. 7 (B, C). As for the remaining concentrations of 0.5 and 1.0 g/L CaO_2, the Ft and QY did not change significantly during treatment with GEF type B. On the contrary, even the lower concentrations enclosed in GEF type C, caused a significant reduction of the Ft values. However, the QY though initially dropped ($t = 24$ h), was partially and completely restored for 1.0 g/L and 0.5 g/L CaO_2, respectively. GEF type A was the least efficient delivery system, since it only caused a slight decrease at the highest applied dose of 2 g/L CaO_2 granules, at $t = 48$ h. Also, its quantum yield remained high throughout the treatment process, as shown in Fig. 6A. Their difference could be explained by the textile properties of each fabric type utilized.

A rise in Ft values can be observed in the first hours of treatment with CaO_2 granules which is explained by the pigmentation release due to cell lysis. Even though the recorded Ft values showed an increase in the first 6 h, the QY significantly declined for the same sampling points. Decline in QY is an indicator of cell destruction as it represents the ability of cells to photosynthesize, thus decline of QY verified that the increase in Ft is due to phycocyanin release whose excitation wavelength falls into the measuring wavelength and not to active photosynthesis pigments. The decline in Ft afterwards is a result of pigments' degradation by the excess or residual oxidant.

During treatment, the concentration of H_2O_2 was monitored through a colorimetric reaction to determine the instantaneous residual oxidant concentration. Even though a noticeable amount of H_2O_2 was quantified during the release experiments by all GEF doses, instantaneous H_2O_2 concentrations at $t = 6$, 24, and 48 h were below 0.5 mg/L showing that the oxidant was rapidly consumed by the contaminant and/or the matrix, during treatment.

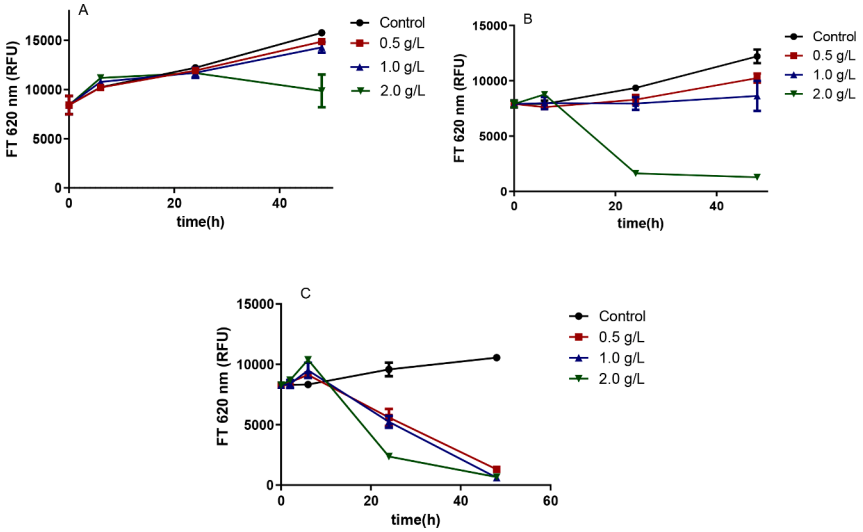

Fig. 6. Effect of 0.5, 1.0, and 2.0 g/L CaO_2 granules enclosed in fabric types (A) pocket lining, (B) interlining textile, (C) polyester netting, on phycocyanin instantaneous fluorescence (Ft) at $\lambda = 620$ nm during the treatment of Microcystis sp. in surface water.

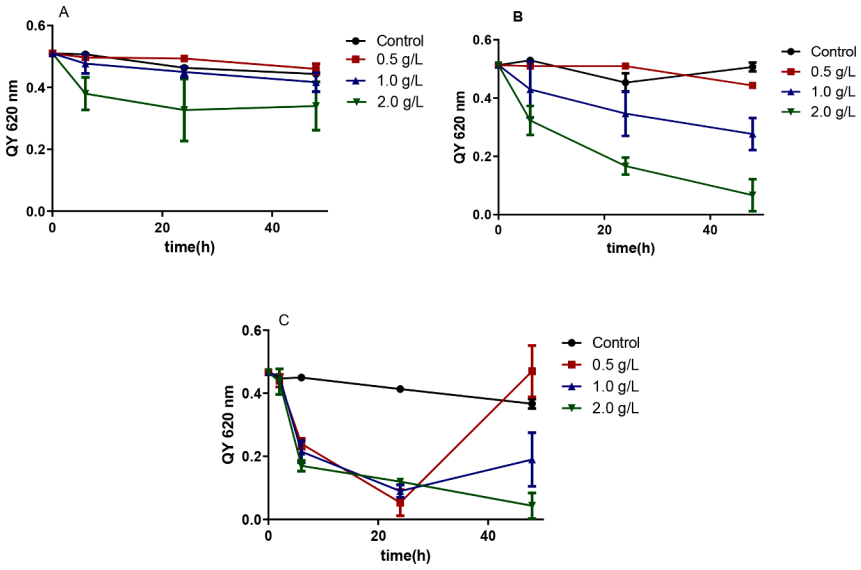

Fig. 7. Effect of 0.0, 0.5, 1.0, and 2.0 g/L CaO_2 granules enclosed in fabric types (A) pocket lining, (B) interlining textile, (C) polyester netting, on the quantum yield of the PSII (QY) at $\lambda = 620$ nm during the treatment of Microcystis sp. in surface water.

3.4.2. *Physicochemical water parameters*

During the treatment experiments, the physicochemical water parameters were monitored to evaluate the effect of GEF systems on matrix pH, conductivity, salinity, and TDS. Matrix pH is one of the most important parameters that required monitoring since it is important to avoid high pH values that caused by released $Ca(OH)_2$ into the waterbody. Fabric type A affected water pH the least, which was 9.5; while type B and C slightly increased the pH around 0.5 units. Still, all the encapsulated systems kept the pH lower or close to 10 while directly applied granules significantly increased the pH above 11 (Fig. 9). Salinity, TDS, and conductivity were found to be within acceptable ranges for freshwater during the treatment, and the Salinity and TDS were found to be the least affected parameters (Figure S4).

4. Discussion

4.1. *H_2O_2 release kinetics by CaO_2 granules and GEF*

The H_2O_2 release curves of each GEF system evaluated in this study, showed that GEF can release comparable H_2O_2 concentrations to the direct application of CaO_2 granules in a surface water. GEF type D, comprising of paper filter and tights, was the only delivery system that had minimal H_2O_2 release and that was probably caused by the reaction of H_2O_2 with the paper and/or its adsorption on the filter, that eventually inhibited its diffusion to the bulk of the solution. In the other three cases (A – C) no paper filter was added along with the fabrics to avoid oxidant permeability issues. Those delivery systems resulted in similar H_2O_2 releasing capacity and followed a pseudo-first order release kinetics model. Even though a linear regression equation was firstly employed to study the release kinetics as proposed by the literature [14, 29], the correlation coefficient ranged between 0.88–0.92 which is considered low. By fitting the curves to a pseudo-first order kinetics model, the correlation coefficients increased to 0.94 – 0.97. Two studies [14, 29] in the cited literature reported a "good fit" to the pseudo-zero-order model for the release of H_2O_2 by CaO_2 granules, which was not compatible with the results as well as with the fact that the release curves reached a distinct plateau after 6 h of release.

The overall released concentration in each GEF was the same ($p > 0.1$), and a linear regression analysis between the added dose and the H_2O_2 yield was obtained. The analysis showed that H_2O_2 yield depends on the CaO_2 dose through a linear relationship ($R^2 = 0.97$–0.98). The obtained linear equation could be a useful tool on deciding on the CaO_2 granules doses during an *in-lake* application based on indications of the overall H_2O_2 requirements. These results confirm previous studies that suggested a linear relationship between the H_2O_2 yield and the added CaO_2 granules dose [16] and support the findings that the release is not following a pseudo-zero-order kinetics model since it was not dose independent.

4.2. *GEF application for Microcystis sp. mitigation*

Treatment of dense *Microcystis* sp. with GEF exhibited various efficiencies on reducing Ft and QY of the PSII. Fabric type A was thicker than the other textiles (Fabric $A = 260 > B = 200 > C = 170$ μm) caused cyanobacteria cells to "adhere" on its external surface, which clogged the pores of the fabric. This may have caused restrictions between the cyanobacteria cells that were in the bulk of the treated water and the oxidant released, which kept the Ft and QY at high levels compared with the other GEF at equivalent treatment times. Fabric type B was quickly submerged into the water sample. This behaviour of the textile material was expected as this type of fabric is generally used as a fusing paper. Being easily submerged from the first hours of treatment allowed better diffusion of oxidant to the water matrix, that caused a high treatment efficiency for the applied dose of 2 g/L. The textile utilized for GEF type C was a water-resistant polyester net, and therefore for the first 6 h it was floating above the surface instead of being submerged into the water matrix. Even though it was not in contact with all the medium, granules were fully submerged into the water that allowed a water exchange between the internal and external of the fabric and hence diffusion of the released H_2O_2 to the bulk was enough to result in effective treatments (Fig. 8).

During the bench-scale experiments, attention was given to ensure that granules were folded as a monolayer inside the fabric material, in order to be totally submerged into the water which allowed their continuous contact through the pores of the material. The percentage of the upper layer of surface water covered by GEF system in the experiments were 5.3%, 14.2%, and 29.5% for GEF 0.5, 1.0, and 2.0 g/L CaO_2 granules, respectively. Based on the obtained results, the surface area of GEF systems applied on the upper layer of surface water (floating on the top) is sufficient to mitigate a dense Chroococcales bloom. Future studies should examine the efficiency of GEF systems on other cyanobacterial species that differ in morphology and bloom type, since the performance of the water treatment system can be greatly affected by these parameters. In the present study, GEF systems were applied on the

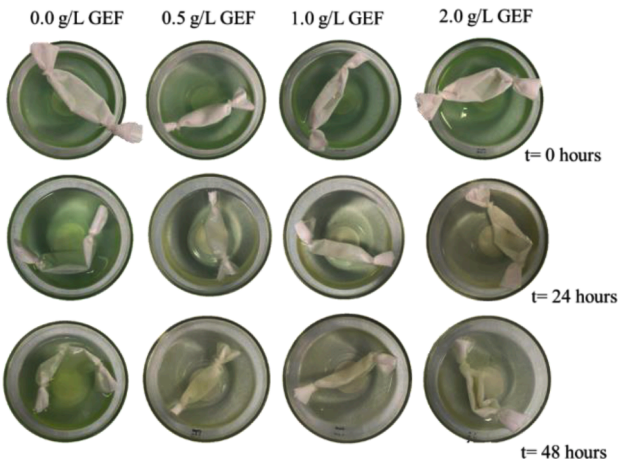

Fig. 8. Treatment of *Microcystis* sp. with GEF in concentrations of 0.0 (control), 0.5, 1.0, and 2.0 g/L CaO_2 granules enclosed in fabric type C, at $t = 0$, 24, and 48 h.

surface, fully submerged into the water and were most of the time static (slow turbulence with a glass rod every hour), as shown in Fig. 8.

Overall, a high dose of 2.0 g/L CaO_2 granules enclosed in textile material was required to fully combat the *Microcystis* species in all tested fabrics. This dose corresponds to an accumulative release of 12 mg/L H_2O_2, meaning that the requirement for liquid H_2O_2 in this case was high. If liquid H_2O_2 was used directly at this high dose, it would probably had cause adverse effects to the remaining aquatic organisms of the waterbody and especially it would have affected the mobility of the zooplankton. Studies showed that H_2O_2 concentrations above 9 mg/L can cause mortalities to *Calanus spp*., a dominant zooplankton species in the North Atlantic [30]. Other studies utilizing liquid H_2O_2 to mitigate *Microcystis* blooms indicated that high H_2O_2 doses (>10 mg/L H_2O_2) are required for their effective treatment [31]. There is a trend to switch to multiple or repeated H_2O_2 doses in order to avoid the single high H_2O_2 dose [32,33], which is costly, time consuming and resources demanding. By applying CaO_2 granules in a controlled manner (e.g., enclosed in materials), the required dose will be released gradually into the waterbody to treat the contaminant, and not directly in high doses. With this mechanism, the instant H_2O_2 concentrations in the waterbody will never or barely exceed lethal doses for fish and other aquatic life.

Results in this study showed that fabrics type B and C enclosing 2.0 g/L (equally to 12 mg/L H_2O_2) resulted in the successful mitigation of *Microcystis* sp. (Figs. 6 and 7). Even though that high dose of granules was added, the instant H_2O_2 concentrations throughout the treatment was lower than 0.5 mg/L, which validates the hypothesis that slow release of the oxidant in combination with its consumption by the contaminants, it will result in low effect on other species due to its less availability. Taking into consideration the insignificant changes on the physicochemical characteristics of the water during treatment with GEF in contrast with the steep increase of pH when granules are applied directly, GEF system can be considered as a safer and more environmentally friendly application method of the granules. This delivery system allowed the release of H_2O_2 through the porous of the fabric material and at the same time the partial restriction of $Ca(OH)_2$ precipitate release into the water matrix. In general, GEF can perform equally successful mitigation as the CaO_2 direct application in surface waters for *Microcystis* mitigation since GEF systems exhibited an H_2O_2 releasing capacity equal to their direct application. The H_2O_2 release by GEF enclosing 2.0 g/L granules, was sufficient to reduce the Ft and QY, and resulted in pH values lower than 10.

As stated previously, pH is also a parameter that needs attention during an *in-situ* chemical treatment, since it disrupts the ecosystem and can potentially make it inappropriate for drinking purposes without costly chemical adjustment of its pH value. The surface area of fabric type C was noticeably higher than the other textiles, which may have caused the partial release of $Ca(OH)_2$ precipitate into the water. The particle size of the $Ca(OH)_2$ powder ranges from 0.5 to 20 μm with the most common ones to be around 15 μm [34]. The pores of material A (16 ± 0.6 μm) could barely limit the release of $Ca(OH)_2$ into the water, while the pores of type B (4 ± 0.3 μm) had higher chances to restrict the release of the powder into the bulk. Differences between the direct application of CaO_2 granules and GEF when 2 g/L were applied can be observed in Fig. 9, where all GEF systems had minimal variations, while direct application caused a steep increase to pH above 11. Since all GEF systems affected pH similarly, it is likely that $Ca(OH)_2$ powder had particle size close to the pores' surface area of the materials, that allowed its capture into the fibre networks, where the knots were.

The present study evaluated both the hydrogen peroxide releasing properties of free and enclosed in fabrics granules as well as their mitigation efficiency when used for the restoration of contaminated with *Microcystis* sp. surface water. Even though the application of an H_2O_2 delivery system allows the removal of persistent contaminants while avoiding the direct application of granules in the environment, attention should be given to the concentration of cyanotoxins prior and following treatment. Intracellular MC-RR and MC-YR were present in the cyanobacteria cells prior oxidant addition, which can be released into the water after cell distraction and lysis. It was proven in previous studies that extracellular-MC are significantly increased with increasing oxidant dose, while the concentration of intracellular-MC is decreased [35]. Based on the above, further experiments should be conducted on the cyanotoxins release and degradation efficiency during treatments utilizing GEF delivery systems.

5. Conclusions

In this study it was proven that granules enclosed in textile materials can obtain similar accumulative H_2O_2 release as their direct application in surface water. Attention was paid on the maximum accumulative H_2O_2 concentrations released by each GEF system utilized in this study. It was shown that the CaO_2 granules in GEFs retained their ability to release H_2O_2 due to the permeability of the porous textile materials used to encapsulated them. Their potency to gradually release oxidant the first 24 h of contact with the water matrix, enhanced the hypothesis that GEF systems can be utilized for surface water treatment applications. Especially in cases were multiple H_2O_2 doses are required for the effective removal of a contaminant, GEF may offer a novel and alternative H_2O_2 delivery system. Based on the above findings, fabrics of nonwoven interline and polyester netting materials can be used as delivery systems, while paper filters should be avoided due to their oxidant adsorption/reacting properties.

The sustainability of the GEFs systems as an alternative to CaO_2 direct application can be elucidated based on their ability to eliminate the exposure of granules into the waterbody and thus minimizing their availability to be consumed by non-targeted species. Also, such delivery systems can be easily removed from the waterbody after the treatment

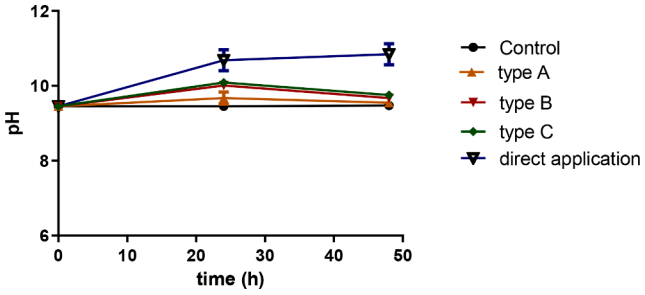

Fig. 9. Changes in pH during treatment of Microcystis sp. in surface water by 2.0 g/L CaO_2 granules direct application and GEF type A – C.

without allowing the accumulation of granules in water and soil and eliminating the need for expensive post treatment.

Though in theory GEF systems have great scalability potential, this should be further tested in up-scale experiments in order to safely propose them for the restoration of contaminated with toxic cyanobacteria waterbodies. Further investigations on the degradation and mitigation efficiencies of GEF systems on cyanotoxins (intra and extra cellular) and other cyanobacterial species, respectively. Finally, scale-up experiments will give concrete proof of the *in-situ* application potential of these eco-friendly H_2O_2 delivery systems.

6. Funding

Funding: This work was supported by the Cyprus Seeds Organization under the project "Novel physico-chemical oxidation processes for mitigating toxic cyanobacterial blooming - CYANOXI" (Grant number N/A).

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.

Acknowledgments

The authors are thankful to the Water Development Department granting access to Kouris dam for sampling and monitoring purposes. Authors are also thankful to the journal reviewers for their insightful input and suggestions that helped us improve significantly the manuscript. Mrs. Keliri is thankful to the Cyprus University of Technology for the tuition waiver (50%) as scholarship for her doctoral studies.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ceja.2022.100318.

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