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Research Paper

Evaluation of algaecide effectiveness of five different oxidants applied on harmful phytoplankton

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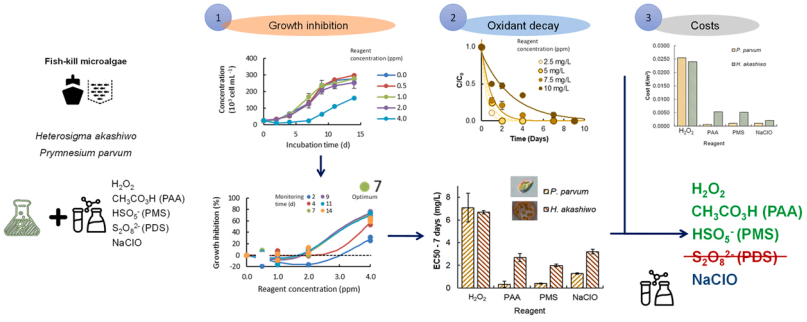
HIGHLIGHTS

- H_2O_2 shows a maintained and similar effect for both *P. parvum* and *H. akashiwo*.
- PMS and PAA exhibit strong but shorter effects although PDS show negligible effect.
- *H. akashiwo* shows higher resistance than *P. parvum*, except when H_2O_2 is used.
- Concentration–response interpretations might be misleading on first incubation days.
- The use of H_2O_2, PAA, or PMS revealed advantageous features if compared to chlorine.

GRAPHICAL ABSTRACT



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ABSTRACT

Harmful algal blooms (HABs) in coastal areas similarly impact both ecosystems and human health. The translocation of phytoplankton species via maritime transport can potentially promote the growth of HABs in coastal systems. Accordingly, ballast water must be disinfected. The main goal of this study is to assess the effectiveness of different emerging biocides, including H_2O_2, peracetic acid (PAA), peroxymonosulfate (PMS), and peroxydisulfate (PDS). The effectiveness of these biocides is compared with that of conventional chlorination methods. Their effects on two ichthyotoxic microalgae with worldwide distribution, i.e., *Prymnesium parvum* and *Heterosigma akashiwo*, are examined. To ensure the prolonged effectiveness of the different reagents, their concentration–response curves for 14 days are constructed and examined. The results suggest a strong but shorter effect by PMS (EC50 = 0.40–1.99 mg·L^{-1}) and PAA (EC50 = 0.32–2.70 mg·L^{-1}), a maintained effect by H_2O_2 (EC50 = 6.67–7.08 mg·L^{-1}), and a negligible effect by PDS. *H. akashiwo* indicates higher resistance than *P. parvum*, except when H_2O_2 is used. Based on the growth inhibition performance and consumption of the reagents as well as a

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review of important aspects regarding their application, using H_2O_2, PAA, or PMS can be a feasible alternative to chlorine-based reagents for inhibiting the growth of harmful phytoplankton.

1. Introduction

The formation of harmful algal blooms (HABs) in coastal areas impose similar effects on both ecosystems and human health. HAB events have increased in frequency, intensity, and geographical distribution over the previous decade [1]. However, the formation of these events is not comprehensively understood. However, anthropogenic factors, such as discharge from wastewater treatment plants, shipping, or aquaculture, have been shown to promote the development of HAB events. Desalination plants or coastal farms can also be affected by these events [2]. Thus, the development of adequate surveillance and management practices is encouraged but remains challenging [3].

The translocation of phytoplanktonic species via maritime transport and ballast water can potentially promote the growth of HABs in coastal systems [4–6]. Although the success of the future establishment of marine species depends on biotic and abiotic factors [7], evidence of ballast water-mediated harmful phytoplankton has been reported globally [8–11]. The international community is aware of this problem and has thus established the International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWMC) [12]. Accordingly, to fulfill biological discharge standards that include phytoplankton species measuring ≥ 10 to < 50 μm (BWMC Rule D2), the implementation of disinfection methods is necessary [13].

In this regard, physical, chemical, and biological processes have been investigated. For example, ultraviolet (UV) irradiation is a well-implemented method; however, one of its main disadvantages is the regrowth of phytoplanktonic organisms [14]. In seawater, chemical disinfection systems, such as electrochemical processes, are applied and have become the second preferred option for ballast water treatment [13]. Nonetheless, only a few studies have investigated their applicability in mitigating HAB species in marine environments.

The correct application and management of chemical reagents is necessary for safe water treatment, as the generation of disinfection byproducts (DBPs) is possible. A clear example is the use of chlorine reagents, which are well-known promoters of DBPs such as trihalomethanes [15,16]. This is similar to ozonation techniques in seawater matrices [17]. In this regard, emerging oxidants with biocidal activity have received increasing attention as potential substitutes for chlorine-based oxidants. For instance, H_2O_2-based reagents are promising environmentally friendly reagents for water disinfection with potential applications in freshwater enclosed lakes [18,19] and aquaculture systems [20,21]. Additionally, persulfate salts have been investigated in recent years, particularly for their role in advanced oxidation processes (AOPs) [22,23], which have mainly been investigated for the removal of *Microcystis aeruginosa* in freshwater [24–26]. However, the specific sensitivity to peroxides (e.g., H_2O_2) for cyanobacterial species over that of other eukaryotic phytoplankton was reported [18,19,27,28], most likely because cyanobacteria display a lower antioxidant activity than eukaryotic algae [28].

In general, studies regarding biocides and their ability to inactivate marine HAB-related species are few. For instance, the application of 100 mg $H_2O_2 \cdot L^{-1}$ has been shown to successfully inhibited the cyst germination of dinoflagellates [29]. Meanwhile, persulfate salts have been applied to two marine species at relatively high concentrations of approximately 610 mg $S_2O_8^{2-} \cdot L^{-1}$ [30]. Notably, the prolonged effectiveness of a chemical treatment can vary depending on whether the assessment is performed for the short or long term, as the consumption of chemicals and the regrowth of microorganisms can occur. The importance of potential subthreshold effects has also recently been highlighted (i.e., hormesis) [31]. In this regard, most previous experiences are assessed for a short term (< 7 days), and the perceptions of chemical effectiveness may vary when assessed for longer durations [32,33]. In this context, Mathijs et al. (2008) performed a comprehensive study by assessing the effectiveness of H_2O_2 for eliminating five different marine species [34]. Gregg and Hallegraeff (2007) reported the effectiveness of three different commercial systems in marine microalgae and reported promising results; however, they suggested that the effective chemical concentrations might be higher for marine species [35].

Therefore, safe and effective methods for controlling harmful phytoplankton in ballast water must be identified urgently. The use of emerging oxidants (peroxides or persulfates) in different water treatment processes, such as AOPs, demonstrates the potential of these chemical reagents for these purposes [23]. The fact that peroxides or persulfates can be produced electrochemically renders these oxidants promising for application [36,37]. To date, the specific biocide effects on undesirable species, such as marine HAB-related species, are limited. Hence, in this study, two environmentally harmful microalgae with worldwide distribution are selected as target microorganisms: *Prymnesium parvum* and *Heterosigma akashiwo*. These golden-brown flagellates are considered active fish-killing HAB species, both of which are included in the IOC-UNESCO Taxonomic Reference List of Harmful MicroAlgae [38]. In addition, they are considered prominent representatives of key HAB species [1,39].

In the case of *P. parvum,* strategies for its management are rarely reported [40], whereas pulsed hydraulic flushing [41], clays or barley straw [42], and specific herbicides [43] are primarily prioritized. For *H. akashiwo*, some technological processes, such as pulsed light or UV radiation, have been investigated [44]. Chemical methods primarily focus on biological-based antialgal compounds [45–47]. However, few studies have been conducted regarding emerging oxidants, such as H_2O_2 in *H. akashiwo* [48] or *P. parvum* [49]. In addition, the effectiveness of applying persulfate salts to *P. parvum* and *H. akashiwo* is unknown.

The main motivation of the present study was to focus on the efficacy of emerging oxidants with biocide activity that are attracting increased attention in Advanced Oxidation Processes, as they can be considered potential substitutes for chlorine-based oxidants. In addition, the present study aims to cover knowledge gaps regarding the prolonged effectiveness of chemical treatment, as the consumption of chemicals and regrowth of microorganisms can occur, and it might vary from short- to long-term assessment. Therefore, the present study is performed to assess the effectiveness of different potential biocides, grouped as peroxides or persulfate salts, on two different marine HAB-related species that differ in size and are thus contemplated by the discharge limit standards established in BWMC [12]. Additionally, the use of traditional chlorine reagents is considered for comparative purposes.

2. Material and methods

2.1. Microalgal cultures and cell growth monitoring

The target organisms were *Prymnesium parvum,* strain BMCC29 (Haptophyta, Carter 1937), and *Heterosigma akashiwo,* strain BMCC76 (Ochrophyta, Hada, Hara & Chihara 1987), which were naturally isolated from Santander Bay and Portugalete (Spain), respectively. They were provided by the Basque Microalgae Culture Collection (BMCC). *Prymnesium parvum* is an euryhaline, icthyotoxic microalga [50] that causes significant global economic losses due to fish kills in aquaculture facilities and fish farms [51,52]. A recent example is the fish mortality event caused by *P. parvum* in the Oder River in the summer of 2022 [53]. Despite their small size (≤ 10 μm), *P. parvum* has been reported as a target organism [54,55] as it can appear, for example, in harbor waters

[10]. *Heterosigma akashiwo* is an icthyotoxic microalga that has been associated with fish kill events in the aquaculture industry for many years [56]. It fits within the size range regulated by the BWMC Rule D2 standards (10–50 μm). Their euryhalitic properties have been shown to facilitate the successful growth of exotic strains in different salinity scenarios [10]; thus, they are promising candidates to be introduced via ballast waters in European countries [5,57].

The strains were maintained and grown in natural seawater from Cádiz Bay from sampling station located at 36°32'33″N; 6°16'44"W (pH = 7.99 ± 0.05; salinity = 36.17 ± 0.19). Sampled water was filtered using Whatman GF/C filters, sterilized, and subsequently enriched with f/2 medium [58]. The cultures were incubated in a culture chamber at 20 °C with illumination supplied by two LED lamps (Phillips LED tube, 18 W, 1600 lm, cool daylight), which provided photosynthetically active radiation of 130 μeinstein·m^{-2}·s^{-1} (QSL-2100 Radiometer, Biospherical Instruments Inc.) at a dark to light cycle ratio of 14:10. All glass materials for microalgal cultures was cleaned in a 10% HCl acid bath, rinsed with distilled water, and then autoclaved at 121 °C.

The cell concentration was determined via fluorescence measurements using a microplate fluorescence reader (Tecan infinite F200; Tecan i-control, 1.6.19.2; plate Corning 96 Flat Bottom White Polystyrol) with an excitation wavelength of 360 nm, emission wavelength of 670 nm, gain of 60, number of flashes of 25, and integration time of 20 μs. Previous analyses indicated that fluorescence is correlated with the cell concentration, determined using a microscope (Leica, DM 750; digital camera Leica, ICC 50 HD) and a Neubauer chamber (Blau Brand). A regression analysis between fluorescence and concentration showed no significant intercept with significant slopes of $1.65 \bullet 10^{-3}$ for *P. parvum* ($R^2 = 0.9953$; n = 28) and $3.59 \bullet 10^{-3}$ for *H. akashiwo* ($R^2 = 0.9816$; n = 20), for concentrations up to $6 \bullet 10^5$ and $4.2 \bullet 10^5$ cell·mL^{-1}, respectively. Fluorescence measurements showed that high sensitivity and accuracy results were obtained, and the fluorescence analysis required a small amount of culture as well as a brief processing time [14]. After adding chemicals to the sample, fluorescence was measured every 2 days. The fluorescence value obtained for each sample was the average of four determinations, with a coefficient of variation of less than 10%.

2.2. Chemical reagents

Five different chemical reagents were used to assess the biocidal efficacy of the two selected strains of harmful phytoplankton. Thus, two peroxides, specifically hydrogen peroxide (H_2O_2, solution 30% w/w, EssentQ®, Scharlab) and peracetic acid, PAA ($C_2H_4O_3$, Merck-Supelco, 38–40%); two persulfate salts, namely sodium peroxydisulfate (PDS, $Na_2S_2O_8$, 98%, PanReac AppliChem) and potassium peroxymonosulfate (PMS, $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5\ K_2SO_4$, Oxone©, Sigma-Aldrich); and sodium hypochlorite (NaClO, solution 15% w/v, EssentQ®, Scharlab) were assessed as conventional biocides for disinfection and ballast water treatment. Some specific information regarding these chemicals is provided in Table S1.

The oxidant consumption was determined based on a colorimetric method for H_2O_2 that is in accordance to the standard method DIN 38402 H15 with titanium (IV) oxysulfate, and the absorbance was measured at 410 nm. PAA was monitored using MQuant® colorimetric test strips. The persulfate salts were monitored at 352 nm for PDS and at 395 nm for PMS based on the protocols proposed by Liang et al. (2008) [59] and Wacławek et al. (2015) [60] using potassium iodide (KI, 99%, Pharmpur, Scharlab). Finally, free chlorine generation was monitored using a multiparameter photometer (Hanna HI83303) and an HI93701-F reagent kit of the same brand.

2.3. Experimental approach

Stock cultures of *P. parvum* and *H. akashiwo* were first grown in 250 mL borosilicate flasks. Subsequently, they were diluted and inoculated into fresh medium in 2000 mL borosilicate flasks at low concentrations of approximately 1000 and 5000 cells·mL^{-1}, respectively. After three days of incubation, the cultures exhibited an exponential growth and achieved a concentration of approximately 10^4 cells·mL^{-1}. The initial concentrations were consistent with those listed in standard protocols such as the Guidelines for Approval of Ballast Water Management Systems (G8) [61], as well as some of the principles established in OECD or ISO guidelines [62,63].

The cultures were subdivided into different subcultures (100 mL), and the individual biocides were dosed at the target concentrations listed on Table S1. For each set of experiments, negative controls (i.e., no biocide addition) were cultivated. After biocide addition, the samples were incubated in a climate room under the same conditions as the pretreatment incubation, and the cell concentration was monitored every 2 days (see Section 2.1) and oxidant decay was monitored daily (see Section 2.2) for 14 d.

2.4. Data treatment

2.4.1. Growth curves, growth inhibition, and effective reagent concentration

First, growth curves for both *P. parvum* and *H. akashiwo* were constructed based on daily monitoring, and specific growth curves were obtained for each microalga and reagent investigated at different concentrations.

Based on the growth curves, the growth rate (d^{-1}) can be obtained using Eq. (1). Second, to calculate the effective concentrations, the areas under the growth curves were integrated (trapezoidal numerical integration method) based on the exposure time of each reagent. By obtaining the difference between the area under the control growth curve (A_C) and the area under the growth curve for each reagent concentration (A_t) on specific incubation days, the growth inhibition can be obtained (Eq. (2)) and subsequently be used as a physiological response [62,64].

$$\mu(d^{-1}) = \frac{Ln(N_t/N_0)}{t_t - t_0} \tag{1}$$

$$Growthinhibition(\%) = \left(\frac{A_C - A_t}{A_C}\right) \cdot 100 \tag{2}$$

The concentration–response curves were fitted using the linear-logistic model proposed by Brain and Cousens (1989) [65], which was later reparametrized by Van Ewijk and Hoekstra, (1993) [66] using a hormesis (subtoxic stimulus) factor. This method has been successfully applied in previous studies [64]. To provide a comprehensive representation of the effects of different reagents, this model was reformulated to represent the growth inhibition (%) as a function of the applied reagent concentration, as shown in Eq. (3).

$$Growthinhibition(\%) = 100 \cdot \left(1 - \frac{1 + f \cdot x}{1 + (2f \cdot x_0 + 1)\left(\frac{x}{x_0}\right)^b}\right) \tag{3}$$

f: hormesis factor ($f = 0$ indicates absence of hormesis).

x: reagent concentration (mg·L^{-1}).

x_0: reagent concentration for obtaining a 50% inhibition (EC50).

b: slope of the curve on logit-log-scale.

EC50 values (x_0) and other relevant parameters, such as the hormesis factor, were obtained by fitting the inhibition percentage obtained using Eq. (2) and the reagent concentrations on specific incubation days. These calculations were performed using SigmaPlot (v11.0; Systat Software Inc. USA). The reagent concentration required to achieve a growth inhibition of 90% (i.e., EC90) was calculated based on the model parameters determined via data fitting. For specific cases, differences between groups were tested using one-way ANOVA, and least significant difference (LSD) test was used to identify significantly different groups.

All the statistical analyses were performed with STATGRAPHICS Centurion (v.16.1.03). Statistical significance was accepted at $p < 0.05$.

2.4.2. Decay of oxidants

The degradation of each reagent showed an exponential decay. Accordingly, the experimental data were fitted to a first-order kinetic model [33,67] using Eq. (4). Thus, the kinetic constant (k, d^{-1}) can be obtained using the measured initial reagent concentration (C_0) and the reagent concentration at a specific time (C_t) measured daily (*t*, d). Additionally, the half-life ($t_{½}$) can be obtained using the equation, $t_{½} = \ln 2/k$. Similarly, the calculations were performed using SigmaPlot (v11.0; Systat Software Inc. USA).

$$Ct = C_0 \cdot e^{-kt} \quad (4)$$

3. Results and discussion

3.1. Reagent effect on growth

The specific growth curves obtained for *P. parvum* and *H. akashiwo* according to the reagents investigated are shown in Fig. 1.

3.1.1. Peroxides

H_2O_2 and PAA were applied in the ranges of 2.5–10 mg·L^{-1} (0.07–0.29 mmol·L^{-1}) and 0.1–2 mg·L^{-1} (1.31–26.30 μmol·L^{-1}), respectively (Figs. 1a-1d).

The effects of H_2O_2 on the growth of *P. parvum* and *H. akashiwo* are shown in Fig. 1a and Fig. 1b. A clear effect was observed when it was applied at a concentration of 5 mg H_2O_2·L^{-1}, where the growth rate of *P. parvum* decreased (Fig. 1a), thus resulting in negative growth rates when 10 mg H_2O_2·L^{-1} was administered (Table S2, Supplementary Material). Similar results were obtained for *H. akashiwo* (Fig. 1b), whose growth rate decreased and was negative when 7.5 and 10 mg H_2O_2·L^{-1} were administered (Table S2). Meanwhile, PAA showed significant effects in a small range of concentrations (Figs. 1c and 1d), particularly in the case of *P. parvum*, whose growth rate remained similar to those of the control samples or decrease significantly to negative values for 0.5 mg PAA·L^{-1} (Table S2).

These differences may be caused by the mechanism of the reagents, which may differ between H_2O_2 and PAA. H_2O_2 can naturally decompose into water and oxygen ($pK_a = 11.62$); however, it can also cause lipid peroxidation and diffuse passively through cell membrane porins by damaging cellular defenses against H_2O_2, thus promoting an internal Fenton-like process [68]. This may inhibit peroxidase activity, metabolic activity, and photosynthesis [68–70]. Consequently, a growth defect caused primarily by reactive oxygen species (ROS) accumulated inside the cell might occur [28,70]. A different mechanism is indicated between eukaryotic microalgae and other photosynthetic microorganisms such as cyanobacteria, because of their insufficiently developed H_2O_2-scavenging processes [28,71]. The results obtained show that both *P. parvum* and *H. akashiwo* can be affected at a concentration > 7.5 mg H_2O_2·L^{-1}. This is consistent with results of previous studies [70,72], where 10 mg H_2O_2·L^{-1} was shown to be an effective concentration for inhibiting the growth of microalgae [32,71,73].

PAA ($pK_a = 8.2$) is a well-known disinfectant reagent that is available as an equilibrium mixture with acetic acid, H_2O_2, and water. This mixture has been reported to be more effective than H_2O_2 [33,69], which is likewise supported by the results obtained for *P. parvum* and *H. akashiwo* in this study. Specifically, concentrations of 2 mg PAA·L^{-1} indicated a significant effect on *P. parvum*, although to a lesser extent on *H. akashiwo*. The low stability (particularly at high pH) and high reactivity of PAA may explain the results obtained [74], where a rapid effect was observed within the initial days. This may be because PAA is easily adsorbed onto the cell membrane and can oxidize sulfhydryl and sulfur bonds, resulting in damage to outer membrane lipoproteins and lipid peroxidation [74,75]. Similar to H_2O_2, PAA passively diffuses into the intracellular domain, causing the inhibition of catalases and DNA denaturation, which can result in an internal Fenton process [69,74–76]. Nonetheless, microalgal cultures can grow in a manner similar to that of the control samples when they are not severely damaged (Figs. 1c and 1d). This may be because PAA releases carboxylic acids as a subproduct, which may result in enhanced growth after PAA decomposition [76].

3.1.2. Persulfates

PMS (HSO_5^-) and PDS ($S_2O_8^{2-}$) as persulfate salts were used in the ranges of 0.1–2 mg·L^{-1} (0.92–18.4 μmol·L^{-1}) and 19.2–192.1 mg·L^{-1} (0.1–1 mmol·L^{-1}), respectively, for HSO_5^- and $S_2O_8^{2-}$ (Fig. 1).

In the case of PMS (HSO_5^-, $pK_a = 9.3$), the algaecide effect differed depending on the target microalgae species. In the case of *P. parvum* (Fig. 1e), a concentration of 0.5 mg HSO_5^-·L^{-1} was required to observe an effect on the growth rate, which was evident at concentrations of 1–2 mg HSO_5^-·L^{-1} (Table S2). By contrast, in the *H. akashiwo* cultures, the effect of HSO_5^- was decreased considerably (Fig. 1f), thus resulting in a slightly reduced growth rate at 2 mg HSO_5^-·L^{-1} (Table S2). By contrast, PDS ($pK_a = -3.5$) failed to inhibit the growth of both *P. parvum* and *H. akashiwo* (Figs. 1g and 1h; Table S2).

HSO_5^- is an acidic oxidant characterized by a high reactivity [77,78]. It causes cell damage, mainly at the extracellular level, through a direct oxidative effect of PMS on the cell wall components via changes in the proteins in cell membranes [77,79]. In addition, its low stability is important in matrices with high salinity, which may involve the generation of chlorine species [80,81]. Thus, a greater effect was observed in marine species than in freshwater species, such as *M. aeruginosa* [77] and *P. subcapitata* [82], which is consistent with the low concentrations required to inhibit the growth of *P. parvum* and *H. akashiwo* (Figs. 1e and 1f).

However, the negligible effect of PDS is consistent with results of previous studies that assessed the effect of PDS in both seawater [27,30] and freshwater species [77,82]. Assuming that these oxidizing agents can diffuse through the cell wall and cause intracellular damage, the high stability of PDS in addition to its higher molecular weight might explain the extremely low efficiency of this reagent [82]. Additionally, the results obtained were consistent with those of previous studies, which suggested that the activity of PDS is effective only if the reagent is activated by an external activation factor, such as UV irradiation or transition metals [27,69].

3.1.3. Chlorine

Sodium hypochlorite has been widely tested as a standard reagent that is widely used as a biocide. It was applied in the range of 0.5–4 mg·L^{-1} (0–0.05 mM) (Fig. 1), which is accordance with the typical dosage in ballast water treatment systems [15,17,83].

The addition of NaClO resulted in rapid hydrolysis and the formation of active chlorine in the form of HOCl or OCl^- (pH dependent). In this case, the effect on the growth rate of the target microalgae was particularly evident at 2–4 mg·L^{-1} (Table S2), with *P. parvum* being the most sensitive species (Fig. 1i). These concentrations are consistent with the results of previous studies, i.e., dosing with an initial chlorine of 1–3 mg·L^{-1} was sufficient to cause cell damage in freshwater *M. aeruginosa* [84] or marine *Chlorella salina* [85]. In this case, cell damage can be related to not only disruption to the cell membrane integrity, but also to intracellular damage affecting chlorophyll autofluorescence, intracellular esterase activity, and primary productivity [69,84,85].

3.2. Effective biocide concentrations

Based on the results presented in the previous section, the modeled concentration–response curves for different numbers of exposure days are presented in Fig. 2, where the growth inhibition of the different

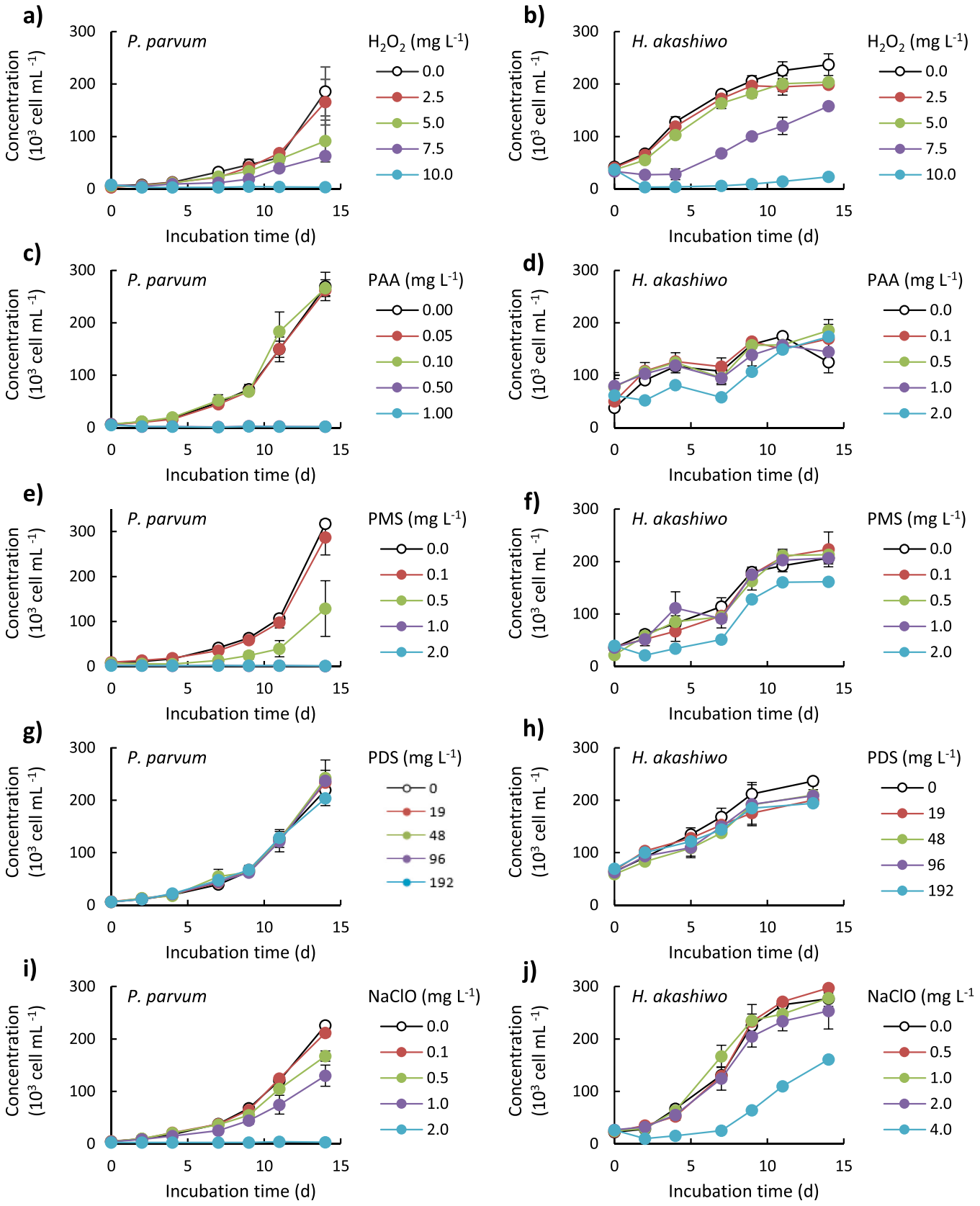

Fig. 1. Growth curves of *Prymnesium parvum* and *Heterosigma akashiwo* after administering different reagents. The reagents used were hydrogen peroxide (H_2O_2), peracetic acid (PAA), peroxymonosulfate (PMS), peroxydisulfate (PDS) and sodium hypochlorite (NaClO).

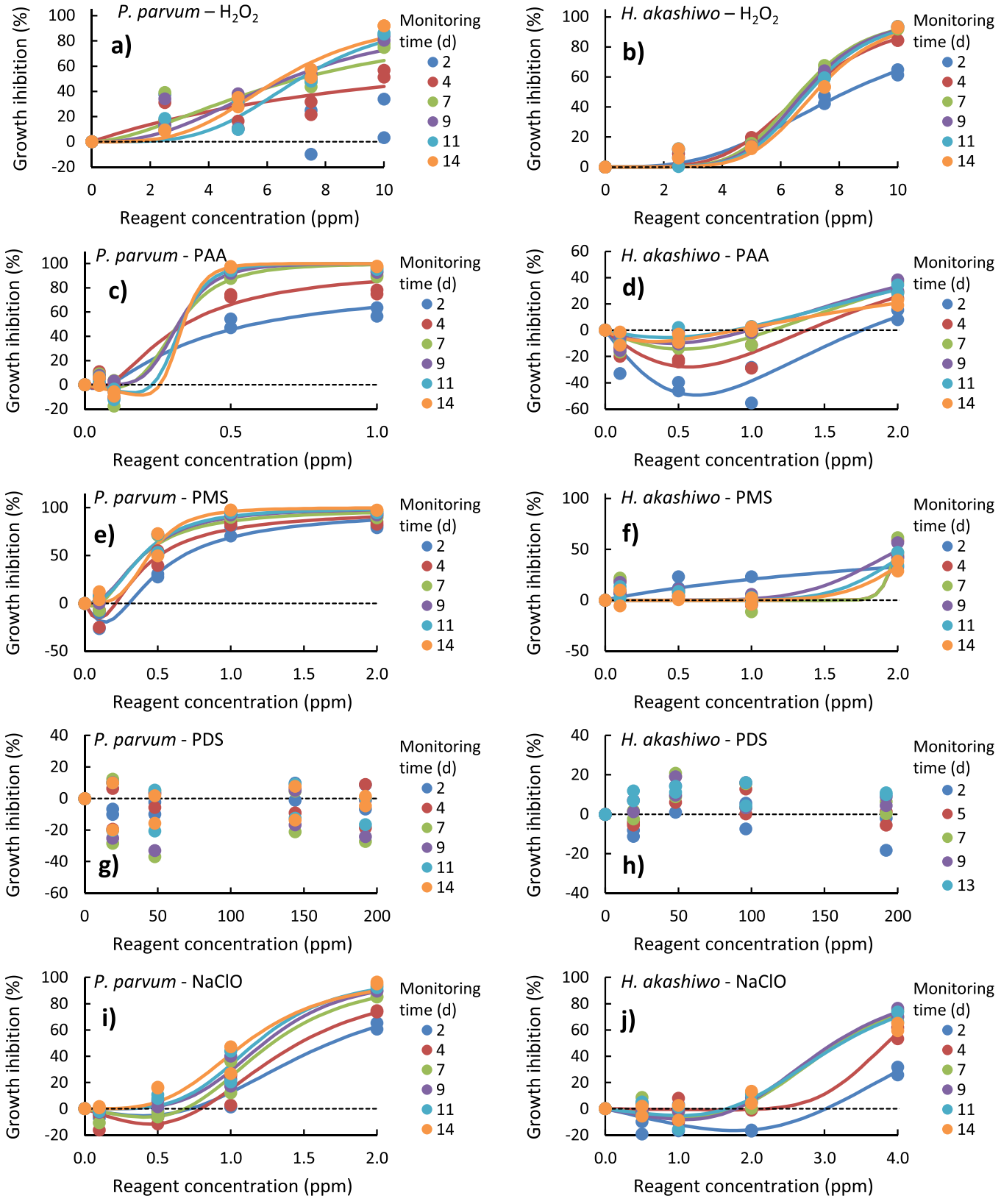

Fig. 2. Concentration–response data of different reagents administered on *P. parvum* and *H. akashiwo* at different incubation times. The reagents used were hydrogen peroxide (H_2O_2), peracetic acid (PAA), peroxymonosulfate (PMS), peroxydisulfate (PDS), and sodium hypochlorite (NaClO).

reagents is addressed. The specific model parameterizations for each incubation day are presented in Table S3 (Supplementary Material).

Regarding H_2O_2 and PAA, their concentration–response curves (Figs. 2a–2d) agreed well with the proposed model. The growth inhibition increased slightly with the H_2O_2 concentration (Figs. 2a and 2b). This implies a clear and sustained effect of H_2O_2 on *P. parvum* and *H. akashiwo*. Based the model, the effects of H_2O_2 were evident beginning from day 7, where the most significant variations were indicate in the first days of incubation (Table S3). However, the inhibition percentage increased significantly for the case of PAA in the range of 0.1–0.5 mg PAA·L^{-1}. This was particularly evident (and maintained) after day 7 of incubation (Fig. 2c). The effects of PAA on *H. akashiwo* cultures decreased considerably (Fig. 2d) and a maximum inhibition percentage of 35% at 2 mg PAA·L^{-1} was indicated. Hormesis was observed on the first day of incubation for PAA concentrations up to 1 mg·L^{-1} (Fig. 2d; Table S3). Based on the results obtained, the estimated EC90 (14 days) values were 11.99 and 10.25 mg H_2O_2·L^{-1} for *P. parvum* and *H. akashiwo*, respectively. For PAA, the EC90 (14 days) was estimated to be 0.75 and 20.57 mg PAA·L^{-1} for *P. parvum* and *H. akashiwo*, respectively. Thus, the different effects of the reagents were clearly determined by the application range (μmol (PAA) vs. mmol (H_2O_2)), which exerted a greater effect for PAA than for H_2O_2. However, this effect was notably reduced by PAA when tested in *H. akashiwo* cultures.

Regarding the persulfates, the observed effect clearly differed between the application of PMS (Figs. 2e and 2f) or PDS (Figs. 2g and 2h). A strong effect on growth inhibition was detected with the use of the PMS, where EC90 (14 days) values were yielded at 0.75 and 2.54 mg HSO_5^-·L^{-1} for *P. parvum* and *H. akashiwo*, respectively. The concentration effect increased gradually and maintained throughout the 14 d of incubation (Fig. 2e). The observable effect at low concentrations was consistent with results of previous studies pertaining to the Chlorophyta *Tetraselmis suecica* [14]. Meanwhile, a negligible effect was observed for PDS; thus, its concentration-response curves could not be modeled (Figs. 2g and 2h).

Finally, by applying NaClO, the estimated EC90 (14 days) values were 2.01 and 7.31 mg NaClO·L^{-1} for *P. parvum* and *H. akasiwo*, respectively. The concentration–response curves (Figs. 2i and 2j) varied slightly depending on the incubation day, where a hormesis effect was indicated at low concentrations in the initial days of incubation. Accordingly, the effects of NaClO effects were evident beginning from day 7 (Table S3).

In general, based the concentration–response curves, the observed effect can vary in the initial incubation days, i.e., days 2 and 4, whereas a similar behavior was shown beginning from day 7 (Fig. 2). In the case of the hormesis factor (f), it is particularly important in the initial days of incubation (e.g., days 2 and 4), specifically for *P. parvum* (PAA, PMS, NaClO) and *H. akashiwo* (PAA, NaClO). Although the hormesis factor is not significant statistically ($p > 0.05$; Table S3), analyzing data for shorter incubation durations might result in incorrect interpretations of the concentration–response curves. Consequently, the associated parameters obtained from modeling the concentration–response curves were similar when they were acquired beginning from day 7 (Table S3) in most cases.

Accordingly, to ensure the homogeneous behavior of the different microalgae upon exposure to the different reagents, the concentration effect on each microalga was considered on day 7. To obtain a general understanding of the effectiveness of each reagent for *P. parvum* and *H. akashiwo*, the EC50 values are obtained, as shown in Fig. 3.

In general, the sensitivity of *P. parvum* was higher than that of *H. akashiwo*, as the EC50 values obtained for the latter were higher, except for H_2O_2 (Fig. 3). As previously discussed, the mechanism of each specific reagent can be related to the different behaviors observed upon exposure to the different reagents; however, the size and physiological characteristics of each specific microalgae should be considered.

Although similar cell concentrations were used at the beginning of the experiment, the size and biovolume for *H. akashiwo* (4187 $μm^3$) were notably higher than those for *P. parvum* (368 $μm^3$) [86]; however, the surface area-to-volume ratios of *H. akashiwo* were smaller than those of P. *parvum*, which implies that *P. parvum* might be exposed more to the oxidizing agent. The biovolume is directly related to the trans-membrane transport mechanisms [87]; therefore, it might imply a faster reagent depletion with less effect on the organisms (see Section 3.3. Oxidant decay). Thus, cells with a larger biovolume are expected to efficiently manage the effect of oxidants, as is the case with *H. akashiwo*.

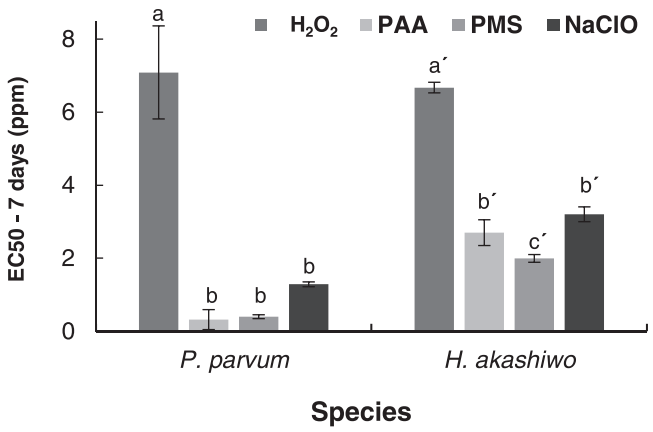

Fig. 3. Reagent concentration for obtaining 50% inhibition (EC50) on *Prymnesium parvum* and *Heterosigma akashiwo* upon exposure to different reagents at day 7 d of incubation. PDS results are not shown as the effects are negligible (see Section 3.1.2.). Different letters represent statistical differences among treatments (one-way ANOVA followed by least significant difference (LSD), $p < 0.05$).

In addition, *H. akashiwo* possesses a glycocalyx as a cell surface structure [88], which may function as a defense against extracellular attack. The glycocalyx is also an enzymatic system responsible for O_2^- generation [89] and thus, the greater production of ROS (e.g., superoxide and O_2^-) in *H. akashiwo* cells compared with that in *P. parvum* has been reported [90]. So, it might imply that *H. akashiwo* would deal more efficiently with oxidative attack by ROS than *P. parvum*.

Based on the effective inhibition of different microalgae, H_2O_2, PMS, and PAA might be promising as algaecides and may be an alternative to conventional chlorination treatments (Fig. 3). However, further studies are recommended to address the possible release of toxins as a consequence of cell lysis after the application of these reagents [73]. Some studies presented promising results with regard to H_2O_2, for which a high efficiency (99.8%) in the abatement of *Alexandrium ostenfeldii* bloom was reported in addition to a reduction in toxin concentrations below regulatory limits [91]. Additionally, Chen et al. (2021) [77], reported that the use of PMS or PDS can decrease the amount of toxins released by *Microcystis aeruginosa* more significantly than H_2O_2. However, the application of these reagents can be a source of highly reactive radicals, e.g., those involved in AOPs, which has demonstrated satisfactory efficiency in the removal of different phycotoxins [92,93].

3.3. Oxidant decay

The degradation profiles of the different reagents used as biocides were monitored over time in microalgal cultures, and the results are shown in Fig. 4. A first-order degradation kinetic model was used for curve fitting, and the derived parameters are listed in Table 1.

Notably, the degradation rates differed between the two species tested. In general, oxidant decay occurred much faster in *H. akashiwo* cultures than in *P. parvum* cultures. In fact, in the *H. akashiwo* cultures, PAA and PMS were completely depleted during the first 24 h; hence, the specific decay rates could not be obtained. Additionally, the degradation rates of the reagents were always lower in the *P. parvum* cultures. This is consistent with the results presented in Section 3.2.

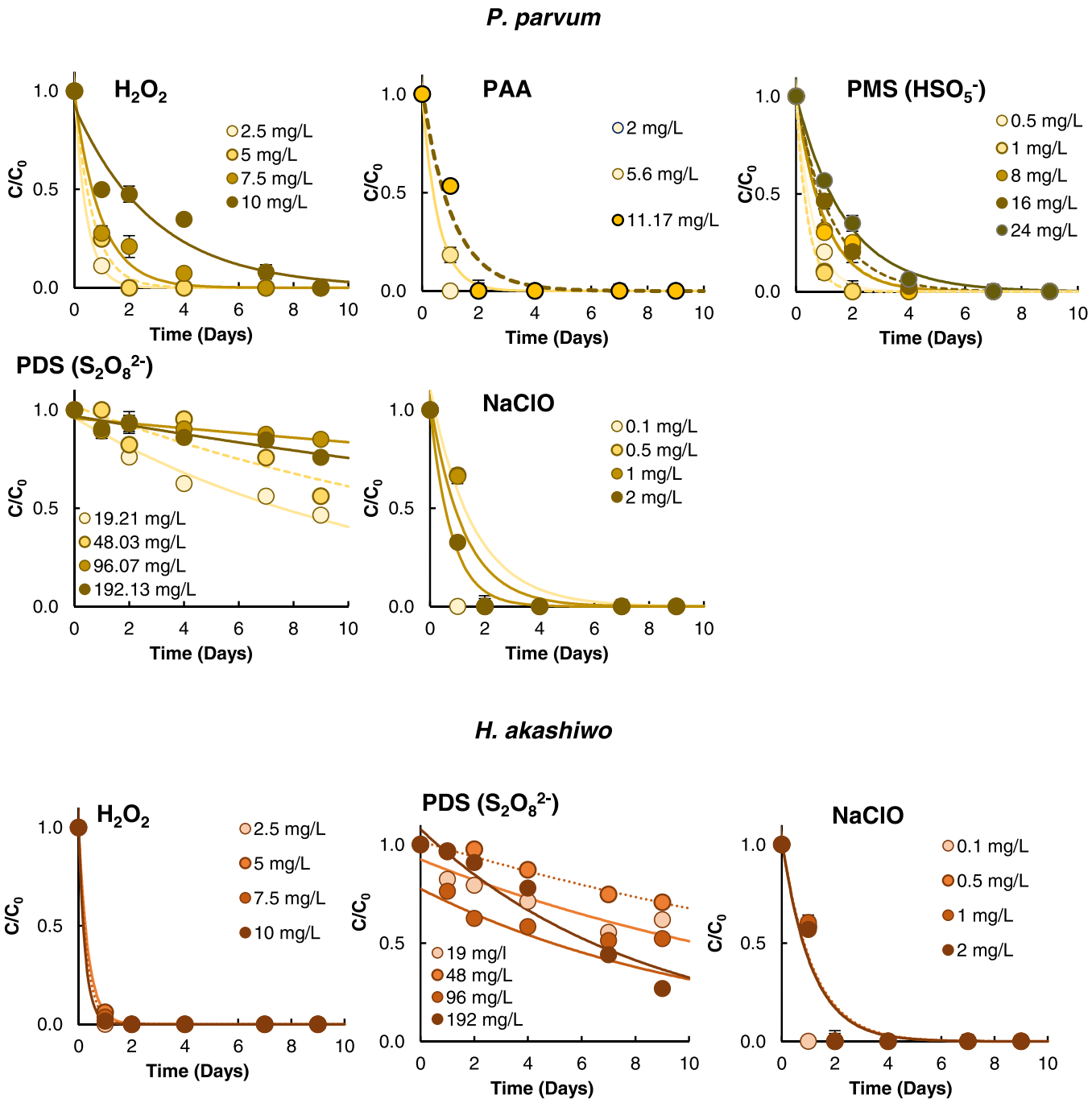

Fig. 4. Oxidant decay in *Prymnesium parvum* and *Heterosigma akashiwo* cultures at different initial reagent concentrations. Symbols represent average reagent concentration with the respective first-order exponential regression fitting represented by lines. *For *H. akashiwo* cultures, PAA and PMS are not represented since rapid depletion was observed.

Dissolved ions and organic matter content in the extracellular environment can stimulate reagent decomposition, whereas the differences in different cultures might be related to the specific production of extracellular polymeric substances (EPSs). Some microalgae generate EPSs, which can serve as a protective buffering layer against biocidal effects as they can neutralize certain reagents such as H_2O_2 [94]. Different microalgae species have different EPS yields and compositions. For instance, *H. akashiwo* has been reported to achieve a high EPS production yield during its exponential growth [95]. In addition, the EPS composition of Phylum Ochrophyta (*H. akashiwo*) differs from that of Haptophyta (*P. parvum*) [95], which might have caused the different depletion rates observed in *H. akashiwo* and *P. parvum* cultures. Concerning the specific reagents, the depletion rate generally decreased as the reagent concentration increased, resulting in higher half-life values with a higher concentration of the reagents, which is consistent with the results of other related studies [33,67]. Except for PDS, a total depletion of all reagents (at effective EC50 values) was obtained during the first 48 h after their addition (Fig. 4, Table 1).

PDS exhibited the lowest degradation rate, which is consistent with its high stability and low reactivity in seawater at the temperatures tested in this study (~20 °C) [30,78]. The low degradation rates and half-lives estimated as 8–27 days (Table 1) are consistent with the

Table 1
Kinetic parameters pertaining to biocide degradation in *P. parvum* or *H. akashiwo* cultures.

Reagent		*P. parvum*			*H. akashiwo*		
		k_{obs} (d^{-1})	$t^{1/2}$ (d)	R^2	k_{obs} (d^{-1})	$t^{1/2}$ (d)	R^2
H_2O_2	2.5 mg·L^{-1}	2.22 ± 0.05	0.312	0.9998	* Consumed < 24 h		
	5 mg·L^{-1}	1.49 ± 0.11	0.464	0.9952	2.82 ± 0.03	0.245	0.9999
	7.5 mg·L^{-1}	1.04 ± 0.15	0.666	0.9719	3.32 ± 0.02	0.208	0.9999
	10 mg·L^{-1}	0.34 ± 0.08	2.015	0.9219	4.14 ± 0.17	0.167	0.9987
PAA	5.6 mg·L^{-1}	1.76 ± 0.02	0.395	0.9984	* Depleted < 24 h		
	11 mg·L^{-1}	0.94 ± 0.21	0.742	0.9393			
PMS	1 mg·L^{-1}	2.31 ± 0.05	0.300	0.9998	* Depleted < 24 h		
	2.5 mg·L^{-1}	2.37 ± 0.06	0.292	0.9999			
	8 mg·L^{-1}	0.97 ± 0.11	0.713	0.9816			
	24 mg·L^{-1}	0.57 ± 0.03	1.215	0.9956			
PDS	19 mg·L^{-1}	0.08 ± 0.01	8.050	0.9476	0.06 ± 0.02	11.63	0.8227
	48 mg·L^{-1}	0.05 ± 0.03	13.56	0.7077	0.04 ± 0.00	16.94	0.965
	144 mg·L^{-1}	0.01 ± 0.01	50.97	0.6979	0.09 ± 0.04	7.72	0.431
	192 mg·L^{-1}	0.02 ± 0.01	27.84	0.8429	0.12 ± 0.02	5.77	0.911
NaClO	0.5 mg·L^{-1}	0.63 ± 0.31	1.094	0.7431	0.88 ± 0.23	0.786	0.922
	1 mg·L^{-1}	0.81 ± 0.24	0.854	0.8907	0.86 ± 0.23	0.804	0.914
	2 mg·L^{-1}	1.27 ± 0.14	0.545	0.9872	0.89 ± 0.23	0.773	0.927

negligible effects obtained for the growth inhibition of both *P. parvum* and *H. akashiwo*; furthermore, these findings imply a low interaction of the reagents with both biotic and abiotic factors in algal cultures.

Meanwhile, the PAA and PMS demonstrated high reactivity with algal cultures, as they showed higher degradation rates with half-lives obtained between 0.4 and 0.7 days for the effective concentrations tested. The rapid degradation of PAA has been previously reported and estimated as $t_{1/2}$ = 1–6 h [33,67]. Furthermore, salinity and organic matter content have been reported to stimulate PAA decomposition [67,96]. This is similar to the case of PMS, where higher decomposition rates have been reported previously [77], particularly at high salinities [81]. Therefore, the high reactivity of both PAA and PMS with organic/inorganic compounds present in microalgal cultures may explain the rapid consumption rates obtained. This is consistent with the growth inhibition results presented in Section 3.2, where biocidal effectiveness was considered high and particularly effective during the first days (Fig. 2). The more rapid consumption of these reagents may explain their relative growth after the first day of exposure.

The decomposition rate of H_2O_2 is expected at $t_{1/2}$ = 4–20 h in surface waters, as it can be consumed because of its reaction with natural organic matter [97]. Nonetheless, the reactivity of H_2O_2 with respect to most organic compounds is much lower than that of PAA [96] or PMS [77]. Notably, H_2O_2 can permeate the cell membranes of microalgae. Thus, a higher consumption rate is expected because of microbiological activity [28,97,98]. The half-life of H_2O_2 in the present study was estimated to be 0.3–2 days for *P. parvum* cultures and 0.1–0.2 days for *H. akashiwo* cultures (Table 1). These results indicate that different microalgae can manage H_2O_2 in different mechanisms. For instance, cyanobacteria species have been reported to be affected by H_2O_2 at ten-fold lower concentrations than those affecting green algae and diatoms [28,71,73]; thus, the decomposition rates of H_2O_2 in cyanobacterial cultures are lower than that in other green algae [28]. Interestingly, faster consumption of H_2O_2 was observed in *H. akashiwo* cultures, which suggests that *H. akashiwo* cells have defenses that are more developed against this reagent. This is consistent with the results of relevant studies, which suggest that although the ichthyotoxic action is not H_2O_2 mediated [99], *H. akashiwo* can manage considerable amounts of H_2O_2 because of its physiological features [47,99,100].

Regarding chlorination, the decomposition rate obtained was similar to that for H_2O_2, where a half-life of $t_{1/2}$ = 0.5–1 days was obtained in the microalgal cultures (Fig. 4, Table 1). These decomposition rates agree well with those obtained in cyanobacterial cultures [84] and can be attributed to both the reaction of chlorine species with microalgal cells and extracellular organic matter, where substituted aromatic moieties are more susceptible to chlorine attack [84]. Moreover, salinity and inorganic compounds can affect chlorine consumption and are critical for the formation of DBPs [15], which is further discussed in Section 3.4.

3.4. Implication of inactivating harmful phytoplankton on field application

In the previous sections, the application and effectiveness of the different oxidants tested in the present study were analyzed. However, important aspects such as the potential DBPs or reagent cost must be considered for their appropriate implementation in actual scenarios.

The generation of toxic DBPs associated with oxidative water disinfection is difficult to avoid [101]. Because their potential formation is strictly associated with the water matrix constituents, the application of oxidants in seawater (with a variable concentration of organic matter) is relevant [83]. Hypochlorite is effective for the abatement of both *P. parvum* (EC90–7 days = 2.61 mg·L^{-1}) and *H. akashiwo* (EC90–7 days = 5.97 mg·L^{-1}). However, at this initial dosage, DBPs are likely to form, in particular brominated and chlorinated DBPs [15,17,69]. Thus, for the tested oxidants, chlorination processes are not recommended in seawater matrices despite their optimum cost efficiency.

Additionally, peroxides have shown satisfactory efficacies with notably higher effects of PAA (EC90–7 days $_{P.\ parvum}$ = 0.58 mg·L^{-1}; EC90–7 days $_{H.\ akashiwo}$ = 28.14 mg·L^{-1}) compared with H_2O_2 (EC90–7 days $_{P.\ parvum}$ = 11.99 mg·L^{-1}; EC90–7 days $_{H.\ akashiwo}$ = 9.86 mg·L^{-1}). However, the potential formation of DBPs by PAA is higher than that by H_2O_2 [69], although to a lesser extent compared with chlorination [17]. Accordingly, although considerably lower amounts of PAA are required to inactivate harmful phytoplankton, the use of H_2O_2 is recommended to avoid the potential formation of DBPs. In fact, the formation of DBPs in PAA solutions can likely be minimized depending on the H_2O_2 ratio, i.e., a higher H_2O_2 proportion in H_2O_2:PAA ratios may limit DBP formation [102,103].

Finally, the use of persulfate salts has been considered effective only for the PMS case (EC90–7 days $_{P.\ parvum}$ = 1.21 mg·L^{-1}; EC90–7 days $_{H.\ akashiwo}$ = 2.01 mg·L^{-1}). Nonetheless, although negligible algicidal effects during PDS application have been reported, trivial DBP formation has been reported after its application as a single oxidant [69]. In the case of PMS, although DBPs may form mainly because of the chlorine species formed from Cl^- oxidized by PMS, results showed that both the DBP level and cytotoxicity in PMS were lower than those in NaClO application [104].

Accordingly, the use of H_2O_2, PMS, or PAA can be an alternative to the use of chlorination and is may be safer in terms of DBP generation, although certain operational (e.g., initial concentration) and

environmental factors (e.g. water matrix constituents) must be specifically assessed to ensure their safe application.

In terms of the practical employment of the reagents, the logistics involved must be considered. The three reagents are commercially available; however, only PMS is provided as a powder, whereas H_2O_2 or PAA are typically provided as liquid solutions. Thus, the transport of these solids is logistically less burdensome for operations in the field than that of liquid solutions. In addition, the explosiveness degree of H_2O_2-based reagents is well known, with consequent hazard to storage [105]. Meanwhile, PMS is easy to store, handle, and transport. However, some oxidants can be electrogenerated, such as H_2O_2 [36], which is advantageous to the logistics. However, a higher cost will be incurred as an entire water treatment system instead of a single reagent administration must be implemented.

Finally, the cost of the promising reagents must be considered. In previous studies that consider the economic analysis of NaClO [106], PAA [23,74], PMS [14,107], and H_2O_2 [14,69,107], the mean price for each reagent was assumed, as shown in Table 2. Accordingly, the most economical reagent is NaClO, with PAA, H_2O_2, and PMS being 6.25, 10.5, and 20.75 times more expensive, respectively. However, according to the target concentrations needed to reach EC50 or EC90 values, PAA and PMS may become alternatives from an economic point of view. The application of H_2O_2 results between 7.4 and 24.8 times more expensive, depending on the target species and the target effective concentration desired (Table 2).

Furthermore, for systems using active compounds, an additional procedure was considered in the case of ballast water system approval (BWMC Guideline 9), which pertains to human health, ship safety, and the aquatic environment [16,108]. In this regard, although the half-life of the respective reagents depends on the target microalgae and initial reagent concentration (Table 1), it has been estimated as 0.17–2.01, 0.30–1.21, and 0.40–0.74 days for the cases involving H_2O_2, PMS, and PAA respectively. Thus, PMS and PAA exhibit some desirable features with respect to H_2O_2 because they can be consumed more rapidly than H_2O_2.

4. Conclusions

In the present study, the feasibility of four emerging reagents, namely Hydrogen peroxide (H_2O_2), Peracetic acid ($C_2H_4O_3$; PAA), Peroxymonosulfate (HSO_5^- PMS), and peroxydisulfate ($S_2O_8^{2-}$ PDS), was tested as an alternative to chlorine reagents (NaClO). The growth inhibition of two harmful phytoplankton species (*Prymnesium parvum* and *Heterosigma akashiwo*) has been addressed together with the decomposition of the reagents in microalgal cultures. Both *P. parvum* and *H. akashiwo* were shown to be suitable as challenging organisms. The following conclusions were obtained:

- Based on the concentration–response curves, the reagent effect can vary in the initial incubation days; thus, analyzing data at shorter incubation times might result in incorrect concentration–response interpretations. Accordingly, to ensure the homogeneous behavior of the target microalgae upon exposure to different chemical reagents, the concentration effect was considered appropriate beyond day 7.
- H_2O_2 demonstrated a moderate efficiency in the growth inhibition of both *P. parvum* and *H. akashiwo*, obtaining a similar effect in both species that is sustained during 14 incubation days. The H_2O_2 was consumed with a half-life of 0.2–0.3 days ($[H_2O_2] = 7.5$ mg·L^{-1}). If compared to chlorination and other reagents tested, H_2O_2 presents some limitations if costs are considered.
- The PAA and PMS showed similar results in the growth inhibition of target microalgae, indicating high effectiveness in the case of *P. parvum*. Otherwise, a higher resistance was observed in the case of *H. akashiwo*. Although the high reactivity and the rapid depletion rates observed (PAA and PMS were depleted within the first 24 h), their effectiveness differ depending on the target species. Due the low effective concentrations observed, PAA and PMS may become alternatives from an economic point of view.
- PDS failed to inhibit the growth of both *P. parvum* and *H. akashiwo*, in addition to exhibiting low degradation rates. Thus, the use of PDS as a single reagent is not recommended for microalgae inhibition.
- The size and physiological characteristics of each specific microalgae might influence on the effectiveness of each reagent addressed. In fact, *H. akashiwo* shows higher resistance than *P. parvum*, except when H_2O_2 is used. The size and biovolume for *H. akashiwo* are higher than those for *P. parvum*. These and other physiological aspects should be further investigated in future studies, as they are important factors to consider when the application of different oxidants is targeted at different phytoplankton communities.

According to the results obtained, the use of H_2O_2, PAA, or PMS demonstrated advantageous features as alternatives to chlorine reagents for the inhibition of harmful phytoplankton, including effectiveness in growth inhibition, efficient reagent depletion, and economic considerations. In addition, any of these reagents (including PDS) are well-known sources of hydroxyl or sulfate radicals in the so-called Advanced Oxidation Processes; thus, their application and further investigation can benefit the development of such AOPs.

Environmental implication

Prymnesium parvum and *Heterosigma akashiwo* are considered harmful phytoplankton (icthyotoxic microalgae) that are responsible for significant economic losses caused by fish kill events within the aquaculture industry. The use of chemical reagents with biocidal action might be applied algae-laden water; thus, we addressed the feasibility of employing four emerging reagents compared with traditional chlorination. These are usually applied in Advanced Oxidation Processes such as hydrogen peroxide, peracetic acid, peroxymonosulfate, or peroxydisulfate salt. Growth inhibition performance and reagent consumption were comprehensively studied. In addition, we considered the potential by-products, costs, and logistics issues that arise with their

Table 2
Price and calculated cost for possible treatment of *P. parvum* or *H. akashiwo* per cubic meter.

Reagent	Unit Price (€/kg)	Active Substance (%)	Target effective concentration	*P. parvum*			*H. akashiwo*		
				Amount of reagent (mg·L^{-1})	Quantity (Kg/m^3)	Cost (€/m^3)	Amount of reagent (mg·L^{-1})	Quantity (Kg/m^3)	Cost (€/m^3)
H_2O_2	1.26	35%	EC50 (7 days)	7.08	0.0202	0.0255	6.67	0.0191	0.0240
			EC90 (7 days)	11.99	0.0343	0.0432	9.86	0.0282	0.0355
PAA	0.75	38%	EC50 (7 days)	0.32	0.0008	0.0006	2.70	0.0071	0.0053
			EC90 (7 days)	0.58	0.0015	0.0011	28.14	0.0741	0.0555
PMS	2.49	96%	EC50 (7 days)	0.40	0.0004	0.0010	1.99	0.0021	0.0052
			EC90 (7 days)	1.21	0.0013	0.0031	2.01	0.0021	0.0052
NaClO	0.12	15%	EC50 (7 days)	1.28	0.0085	0.0010	2.62	0.0175	0.0021
			EC90 (7 days)	3.20	0.0213	0.0026	5.97	0.0398	0.0048

environmental application.

CRediT authorship contribution statement

Javier Moreno-Andrés: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing, Funding acquisition, Project administration; **Leonardo Romero-Martínez:** Investigation, Methodology, Formal analysis, Writing - original draft, Writing - review & editing; **Sergio Seoane:** Resources, Writing - review & editing; **Asunción Acevedo-Merino:** Supervision, Writing - review & editing; **Ignacio Moreno-Garrido:** Resources, Writing - review & editing**; Enrique Nebot:** Conceptualization, Formal analysis, Supervision, Writing - review & editing, Funding acquisition.

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

Data will be made available on request.

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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.jhazmat.2023.131279.

References

[1] Wells, M.L., Karlson, B., Wulff, A., Kudela, R., Trick, C., Asnaghi, V., et al., 2020. Future HAB science: directions and challenges in a changing climate. Harmful Algae 91, 101632. https://doi.org/10.1016/J.HAL.2019.101632.
[2] Trottet, A., George, C., Drillet, G., Lauro, F.M., 2021. Aquaculture in coastal urbanized areas: a comparative review of the challenges posed by Harmful Algal Blooms. Crit Rev Environ Sci Technol 1–42. https://doi.org/10.1080/10643389.2021.1897372.
[3] Zhan, M., Liu, P., Liu, X., Hong, Y., Xie, X., 2021. Inactivation and removal technologies for algal-bloom control: advances and challenges. Curr Pollut Rep 1–15. https://doi.org/10.1007/s40726-021-00190-8.
[4] Smayda, T.J., 2007. Reflections on the ballast water dispersal-harmful algal bloom paradigm. Harmful Algae 6, 601–622. https://doi.org/10.1016/j.hal.2007.02.003.
[5] Ardura, A., Borrell, Y.J., Fernández, S., González Arenales, M., Martínez, J.L., Garcia-Vazquez, E., 2020. Nuisance algae in ballast water facing international conventions. Insights from DNA metabarcoding in ships arriving in bay of biscay. Water 12, 2168. https://doi.org/10.3390/w12082168.
[6] Wang, Q., Lin, L., Chen, X., Wu, W., Wu, H., 2022. Transportation of bloom forming species in ballast water by commercial vessels at Yangshan deep water port. Ocean Coast Manag 219, 106045. https://doi.org/10.1016/J.OCECOAMAN.2022.106045.
[7] González-Ortegón, E., Moreno-Andrés, J., 2021. Anthropogenic modifications to estuaries facilitate the invasion of non-native species. Processes 9, 740. https://doi.org/10.3390/pr9050740.
[8] Hallegraeff, G.M., 1998. Transport of toxic dinoflagellates via ships' ballast water: bioeconomic risk assessment and efficacy of possible ballast water management strategies. Mar Ecol Prog Ser 168, 297–309. https://doi.org/10.3354/meps168297.
[9] Mozetič, P., Cangini, M., Francé, J., Bastianini, M., Bernardi Aubry, F., Bužančić, M., et al., 2019. Phytoplankton diversity in Adriatic ports: Lessons from the port baseline survey for the management of harmful algal species. Mar Pollut Bull 147, 117–132. https://doi.org/10.1016/j.marpolbul.2017.12.029.
[10] Butrón, A., Orive, E., Madariaga, I., 2011. Potential risk of harmful algae transport by ballast waters: the case of Bilbao Harbour. Mar Pollut Bull 62, 747–757. https://doi.org/10.1016/j.marpolbul.2011.01.008.
[11] Pertola, S., Faust, M.A., Kuosa, H., 2006. Survey on germination and species composition of dinoflagellates from ballast tanks and recent sediments in ports on the South Coast of Finland, North-Eastern Baltic Sea. Mar Pollut Bull 52, 900–911. https://doi.org/10.1016/J.MARPOLBUL.2005.11.028.
[12] IMO, International Convention for the Control and Management of Ships' Ballast Water and Sediments. BWM/CONF/36., (2004).
[13] Hess-Erga, O.-K., Moreno-Andrés, J., Enger, Ø., Vadstein, O., 2019. Microorganisms in ballast water: disinfection, community dynamics, and implications for management. Sci Total Environ 657, 704–716. https://doi.org/10.1016/J.SCITOTENV.2018.12.004.
[14] Romero-Martínez, L., Rivas-Zaballos, I., Moreno-Andrés, J., Moreno-Garrido, I., Acevedo-Merino, A., Nebot, E., 2021. Improving the microalgae inactivating efficacy of ultraviolet ballast water treatment in combination with hydrogen peroxide or peroxymonosulfate salt. Mar Pollut Bull 162, 111886. https://doi.org/10.1016/j.marpolbul.2020.111886.
[15] Moreno-Andrés, J., Peperzak, L., 2019. Operational and environmental factors affecting disinfection byproducts formation in ballast water treatment systems. Chemosphere 232, 496–505. https://doi.org/10.1016/J.CHEMOSPHERE.2019.05.152.
[16] David, M., Linders, J., Gollasch, S., David, J., 2018. Is the aquatic environment sufficiently protected from chemicals discharged with treated ballast water from vessels worldwide? – a decadal environmental perspective and risk assessment. Chemosphere 207, 590–600. https://doi.org/10.1016/j.chemosphere.2018.05.136.
[17] Shah, A.D.D., Liu, Z.-Q.Q., Salhi, E., Höfer, T., Werschkun, B., Von Gunten, U., et al., 2015. Formation of disinfection by-products during ballast water treatment with ozone, chlorine, and peracetic acid: influence of water quality parameters. Environ Sci Water Res Technol 1, 465–480. https://doi.org/10.1039/c5ew00061k.
[18] Matthijs, H.C.P., Visser, P.M., Reeze, B., Meeuse, J., Slot, P.C., Wijn, G., et al., 2012. Selective suppression of harmful cyanobacteria in an entire lake with hydrogen peroxide. Water Res 46, 1460–1472. https://doi.org/10.1016/j.watres.2011.11.016.
[19] Lusty, M.W., Gobler, C.J., 2020. The efficacy of hydrogen peroxide in mitigating cyanobacterial blooms and altering microbial communities across four lakes in NY, USA. Toxins (Basel) 12, 428. https://doi.org/10.3390/toxins12070428.
[20] Pedersen, L.-F., Pedersen, P.B., 2012. Hydrogen peroxide application to a commercial recirculating aquaculture system. Aquac Eng 46, 40–46. https://doi.org/10.1016/J.AQUAENG.2011.11.001.
[21] Liu, D., Behrens, S., Pedersen, L.F., Straus, D.L., Meinelt, T., 2016. Peracetic acid is a suitable disinfectant for recirculating fish-microalgae integrated multi-trophic aquaculture systems. Aquac Rep 4, 136–142. https://doi.org/10.1016/j.aqrep.2016.09.002.
[22] Lee, J., Von Gunten, U., Kim, J.H., 2020. Persulfate-based advanced oxidation: critical assessment of opportunities and roadblocks. Environ Sci Technol 54, 3064–3081. https://doi.org/10.1021/acs.est.9b07082.
[23] Kiejza, D., Kotowska, U., Polińska, W., Karpińska, J., 2021. Peracids - new oxidants in advanced oxidation processes: the use of peracetic acid, peroxymonosulfate, and persulfate salts in the removal of organic micropollutants of emerging concern – a review. Sci Total Environ 790, 148195. https://doi.org/10.1016/j.scitotenv.2021.148195.
[24] Song, Q., Niu, X., Zhang, D., Song, X., Li, Y., Ma, J., et al., 2020. The behaviors of Microcystis aeruginosa and microcystins during the Fe2+/persulfate (PS) preoxidation-coagulation and flocs storage period. Environ Res 186, 109549. https://doi.org/10.1016/j.envres.2020.109549.
[25] Zheng, X., Niu, X., Zhang, D., Ye, X., Ma, J., Lv, M., et al., 2022. Removal of Microcystis aeruginosa by natural pyrite-activated persulfate: Performance and the significance of iron species. Chem Eng J 428, 132565. https://doi.org/10.1016/J.CEJ.2021.132565.
[26] Qiu, Y., Luo, Y., Zhang, T., Du, X., Wang, Z., Liu, F., et al., 2021. Comparison between permanganate pre-oxidation and persulfate/iron(II) enhanced coagulation as pretreatment for ceramic membrane ultrafiltration of surface water contaminated with manganese and algae. Environ Res 196, 110942. https://doi.org/10.1016/j.envres.2021.110942.
[27] Moreno-Andrés, J., Rivas-Zaballos, I., Acevedo-Merino, A., Nebot, E., 2022. On the efficacy of H2O2 or S2O82- at promoting the inactivation of a consortium of cyanobacteria and bacteria in algae-laden water. Microorganisms 10, 735. https://doi.org/10.3390/MICROORGANISMS10040735.
[28] Weenink, E.F.J., Matthijs, H.C.P., Schuurmans, J.M., Piel, T., van Herk, M.J., Sigon, C.A.M., et al., 2021. Interspecific protection against oxidative stress: green algae protect harmful cyanobacteria against hydrogen peroxide. Environ Microbiol 23, 2404–2419. https://doi.org/10.1111/1462-2920.15429.
[29] Wang, Z., Liang, W., Guo, X., Liu, L., 2018. Inactivation of Scrippsiella trochoidea cysts by different physical and chemical methods: Application to the treatment of ballast water. Mar Pollut Bull 126, 150–158. https://doi.org/10.1016/j.marpolbul.2017.11.002.
[30] Ahn, S., Peterson, T.D., Righter, J., Miles, D.M., Tratnyek, P.G., 2013. Disinfection of ballast water with iron activated persulfate. Environ Sci Technol 47, 11717–11725. https://doi.org/10.1021/es402508k.
[31] Agathokleous, E., Barceló, D., Aschner, M., Azevedo, R.A., Bhattacharya, P., Costantini, D., et al., 2022. Rethinking subthreshold effects in regulatory

chemical risk assessments. Environ Sci Technol 56, 11095–11099. https://doi.org/10.1021/acs.est.2c02896.
[32] Buley, R.P., Adams, C., Belfiore, A.P., Fernandez-Figueroa, E.G., Gladfelter, M.F., Garner, B., et al., 2021. Field evaluation of seven products to control cyanobacterial blooms in aquaculture. Environ Sci Pollut Res 28, 29971–29983. https://doi.org/10.1007/S11356-021-12708-0.
[33] Chhetri, R.K., Baun, A., Andersen, H.R., 2017. Algal toxicity of the alternative disinfectants performic acid (PFA), peracetic acid (PAA), chlorine dioxide (ClO2) and their by-products hydrogen peroxide (H2O2) and chlorite (ClO2−). Int J Hyg Environ Health 220, 570–574. https://doi.org/10.1016/J.IJHEH.2016.11.011.
[34] Mathijs, G.D., Robbert, G., Mark, A.J., 2008. Time and concentration dependency in the potentially affected fraction of species: the case of hydrogen peroxide treatment of ballast water. Environ Toxicol Chem 27, 746–753.
[35] Gregg, M.D., Hallegraeff, G.M., 2007. Efficacy of three commercially available ballast water biocides against vegetative microalgae, dinoflagellate cysts and bacteria. Harmful Algae 6, 567–584. https://doi.org/10.1016/j.hal.2006.08.009.
[36] Petrucci, E., Di Palma, L., De Luca, E., Massini, G., 2013. Biocides electrogeneration for a zero-reagent on board disinfection of ballast water. J Appl Electrochem 43, 237–244. https://doi.org/10.1007/s10800-012-0507-0.
[37] Moreira, F.C., Boaventura, R.A.R., Brillas, E., Vilar, V.J.P., 2017. Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. Appl Catal B Environ 202, 217–261. https://doi.org/10.1016/j.apcatb.2016.08.037.
[38] Moestrup, Ø. , Akselmann-Cardella, R. , Churro, C. , Fraga, S. , Iwataki, H. M., M. , Larsen, J. , Lundholm, N. , Zingone, A. IOC-UNESCO Taxonomic Reference List of Harmful Micro Algae.
[39] Allaf, M.M., Trick, C.G., 2021. Yeast cell as a bio-model for measuring the toxicity of fish-killing flagellates. Toxins 2021 Vol. 13 (13), 821. https://doi.org/10.3390/TOXINS13110821.
[40] Barkoh, A., Smith, D.G., Southard, G.M., 2010. Prymnesium parvum control treatments for fish hatcheries, JAWRA. J Am Water Resour Assoc 46, 161–169. https://doi.org/10.1111/j.1752-1688.2009.00400.x.
[41] Schwierzke-Wade, L., Roelke, D.L., Brooks, B.W., Grover, J.P., Valenti, T.W., 2011. Prymnesium parvum bloom termination: role of hydraulic dilution. J Plankton Res 33, 309–317. https://doi.org/10.1093/PLANKT/FBQ108.
[42] Hagström, J.A., Sengco, M.R., Villareal, T.A., 2010. Potential methods for managing prymnesium parvum blooms and toxicity, with emphasis on clay and barley straw: a review1. JAWRA J Am Water Resour Assoc 46, 187–198. ⟨https://onlinelibrary.wiley.com/doi/full/10.1111/j.1752-1688.2009.00402.x⟩.
[43] Umphres, G.D., Roelke, D.L., Netherland, M.D., 2012. A chemical approach for the mitigation of Prymnesium parvum blooms. Toxicon 60, 1235–1244. https://doi.org/10.1016/J.TOXICON.2012.08.006.
[44] Feng, D., Shi, J., Sun, D., 2015. Inactivation of microalgae in ballast water with pulse intense light treatment. Mar Pollut Bull 90, 299–303. https://doi.org/10.1016/j.marpolbul.2014.09.006.
[45] Quan, H., Zhang, Y., Yin, P., Zhao, L., 2021. Effects of two algicidal substances, ortho-tyrosine and urocanic acid, on the growth and physiology of Heterosoigma akashiwo. Environ Pollut 284, 117004. https://doi.org/10.1016/j.envpol.2021.117004.
[46] Ying Sun, Y., Zhou, J., Han, X., Sheng Zhang, N., Xuan Yang, Z., Zhang, X., 2021. Several natural products isolated from a red alga Gracilaria lemaneiformis and its evaluation of antialgal activity against six common red tide microalgae. Environ Sci Pollut Res 1–18. https://doi.org/10.1007/s11356-020-11755-3.
[47] Zhang, S., Zheng, W., Wang, H., 2020. Physiological response and morphological changes of Heterosigma akashiwo to an algicidal compound prodigiosin. J Hazard Mater 385, 121530. https://doi.org/10.1016/J.JHAZMAT.2019.121530.
[48] Gregg, M., Rigby, G., Hallegraeff, G.M., 2009. Review of two decades of progress in the development of management options for reducing or eradicating phytoplankton, zooplankton and bacteria in ship's ballast water. Aquat Invasions 4, 521–565. https://doi.org/10.3391/ai.2009.4.3.14.
[49] Wagstaff, B.A., Pratscher, J., Rivera, P.P.L., Hems, E.S., Brooks, E., Rejzek, M., et al., 2021. Assessing the toxicity and mitigating the impact of harmful prymnesium blooms in eutrophic waters of the norfolk broads. Environ Sci Technol 55, 16538–16551. https://doi.org/10.1021/ACS.EST.1C04742.
[50] Richardson, E.T., Patiño, R., 2021. Growth of the harmful alga, Prymnesium parvum (Prymnesiophyceae), after gradual and abrupt increases in salinity. J Phycol. https://doi.org/10.1111/jpy.13172.
[51] Johnsen, T.M., Eikrem, W., Olseng, C.D., Tollefsen, K.E., Bjerknes, V., 2010. Prymnesium parvum: the norwegian experience. JAWRA J Am Water Resour Assoc 46, 6–13. https://doi.org/10.1111/J.1752-1688.2009.00386.X.
[52] Roelke, D.L., Barkoh, A., Brooks, B.W., Grover, J.P., Hambright, K.D., LaClaire, J. W., et al., 2015. A chronicle of a killer alga in the west: ecology, assessment, and management of Prymnesium parvum blooms. Hydrobiol 2015 7641 (764), 29–50. https://doi.org/10.1007/S10750-015-2273-6.
[53] Marchowski, D., Ławicki, Ł., 2023. Unprecedented mass mortality of aquatic organisms in the River Oder, 9–9 Oryx 57. https://doi.org/10.1017/S0030605322001387.
[54] Soler-Figueroa, B.M., Fontaine, D.N., Carney, K.J., Ruiz, G.M., Tamburri, M.N., 2020. Characteristics of global port phytoplankton and implications for current ballast water regulations. Mar Pollut Bull 155, 111165. https://doi.org/10.1016/j.marpolbul.2020.111165.
[55] Swackhamer, D. , Meyer, J. , Efficacy of Ballast Water Treatment Systems: a Report by the EPA Science Advisory Board, (2011). https://doi.org/10.1038/cr.1997.15.
[56] Powers, L., Creed, I.F., Trick, C.G., 2012. Sinking of Heterosigma akashiwo results in increased toxicity of this harmful algal bloom species. Harmful Algae 13, 95–104. https://doi.org/10.1016/J.HAL.2011.10.007.
[57] Karlson, B., Andersen, P., Arneborg, L., Cembella, A., Eikrem, W., John, U., et al., 2021. Harmful algal blooms and their effects in coastal seas of Northern Europe. Harmful Algae, 101989. https://doi.org/10.1016/j.hal.2021.101989.
[58] Guillard, R.R.L., Ryther, J.H., 1962. Studies of marine planktonic diatoms. I. Cyclotella nana hustedt, and Detonula confervacea (CLEVE). Canadian. J Microbiol 8:229-239, Can J Microbiol 8, 229–239.
[59] Liang, C., Huang, C.F., Mohanty, N., Kurakalva, R.M., 2008. A rapid spectrophotometric determination of persulfate anion in ISCO. Chemosphere 73, 1540–1543. https://doi.org/10.1016/j.chemosphere.2008.08.043.
[60] Wacławek, S., Grübel, K., Černík, M., 2015. Simple spectrophotometric determination of monopersulfate. Spectrochim Acta - Part A Mol Biomol Spectrosc 149, 928–933. https://doi.org/10.1016/j.saa.2015.05.029.
[61] IMO, 2016. Guidelines for approval of ballast water management systems (G8), Resolut. MEPC.279(70). MEPC 70/18.
[62] OECD, OECD Guidelines for testing of chemicals, Paris, France, 1996.
[63] ISO, Marine algal growth inhibition test with Skeletonema sp. and Phaeodactylum tricornutum, UNE EN ISO 102532006. (2017).
[64] Cho, C.W., Jeon, Y.C., Pham, T.P.T., Vijayaraghavan, K., Yun, Y.S., 2008. The ecotoxicity of ionic liquids and traditional organic solvents on microalga Selenastrum capricornutum. Ecotoxicol Environ Saf 71, 166–171. https://doi.org/10.1016/J.ECOENV.2007.07.001.
[65] Brain, P., Cousens, R., 1989. An equation to describe dose responses where there is stimulation of growth at low doses. Weed Res 29, 93–96. https://doi.org/10.1111/J.1365-3180.1989.TB00845.X.
[66] Van Ewijk, P.H., Hoekstra, J.A., 1993. Calculation of the EC50 and its confidence interval when subtoxic stimulus is present. Ecotoxicol Environ Saf 25, 25–32. https://doi.org/10.1006/EESA.1993.1003.
[67] Pedersen, L., Lazado, C., 2020. Decay of peracetic acid in seawater and implications for its chemotherapeutic potential in aquaculture. Aquac Environ Interact 12, 153–165. https://doi.org/10.3354/aei00354.
[68] Pulgarin, A., Giannakis, S., Pulgarin, C., Ludwig, C., Refardt, D., 2020. A novel proposition for a citrate-modified photo-Fenton process against bacterial contamination of microalgae cultures. Appl Catal B Environ 265, 118615. https://doi.org/10.1016/j.apcatb.2020.118615.
[69] Farinelli, G., Giagnorio, M., Ricceri, F., Giannakis, S., Tiraferri, A., 2021. Evaluation of the effectiveness, safety, and feasibility of 9 potential biocides to disinfect acidic landfill leachate from algae and bacteria. Water Res 191, 116801. https://doi.org/10.1016/j.watres.2020.116801.
[70] Zhang, H., Zong, R., He, H., Huang, T., 2022. Effects of hydrogen peroxide on Scenedesmus obliquus: cell growth, antioxidant enzyme activity and intracellular protein fingerprinting. Chemosphere 287, 132185. https://doi.org/10.1016/J.CHEMOSPHERE.2021.132185.
[71] Drábková, M., Matthijs, H.C.P., Admiraal, W., Maršálek, B., 2007. Selective effects of H2O2 on cyanobacterial photosynthesis. Photosynthetica 45, 363–369. https://doi.org/10.1007/s11099-007-0062-9.
[72] Randhawa, V., Thakkar, M., Wei, L., 2012. Applicability of hydrogen peroxide in brown tide control – culture and microcosm studies. PLoS One 7, e47844. https://doi.org/10.1371/JOURNAL.PONE.0047844.
[73] Kibuye, F.A., Zamyadi, A., Wert, E.C., 2020. A critical review on operation and performance of source water control strategies for cyanobacterial blooms: Part I-chemical control methods. Harmful Algae 109, 102099. https://doi.org/10.1016/J.HAL.2021.102099.
[74] Kitis, M., 2004. Disinfection of wastewater with peracetic acid: a review. Environ Int 30, 47–55. https://doi.org/10.1016/S0160-4120(03)00147-8.
[75] Sun, P., Zhang, T., Mejia-Tickner, B., Zhang, R., Cai, M., Huang, C.H., 2018. Rapid disinfection by peracetic acid combined with UV irradiation. Environ Sci Technol Lett 5, 400–404. https://doi.org/10.1021/acs.estlett.8b00249.
[76] Ao, X., Eloranta, J., Huang, C.H., Santoro, D., Jun Sun, W., Dong Lu, Z., et al., 2021. Peracetic acid-based advanced oxidation processes for decontamination and disinfection of water: a review. Water Res 188, 116479. https://doi.org/10.1016/j.watres.2020.116479.
[77] Chen, Z., Li, J., Chen, M., Koh, K.Y., Du, Z., Gin, K.Y.H., et al., 2021. Microcystis aeruginosa removal by peroxides of hydrogen peroxide, peroxymonosulfate and peroxydisulfate without additional activators. Water Res 201, 117263. https://doi.org/10.1016/J.WATRES.2021.117263.
[78] Wacławek, S., Lutze, H.V., Grübel, K., Padil, V.V.T., Černík, M., Dionysiou, D.D., 2017. Chemistry of persulfates in water and wastewater treatment: a review. Chem Eng J 330, 44–62. https://doi.org/10.1016/j.cej.2017.07.132.
[79] Berruti, I., Oller, I., Polo-López, M.I., 2021. Direct oxidation of peroxymonosulfate under natural solar radiation: accelerating the simultaneous removal of organic contaminants and pathogens from water. Chemosphere 279, 130555. https://doi.org/10.1016/j.chemosphere.2021.130555.
[80] Delcomyn, C.A., Bushway, K.E., Henley, M.V., 2006. Inactivation of biological agents using neutral oxone-chloride solutions. Environ Sci Technol 40, 2759–2764. https://doi.org/10.1021/ES052146.
[81] Wen, G., Zhao, D., Xu, X., Chen, Z., Huang, T., Ma, J., 2019. Inactivation of fungi from four typical genera in groundwater using PMS/Cl−system: efficacy, kinetics and mechanisms. Chem Eng J 357, 567–578. https://doi.org/10.1016/j.cej.2018.09.195.
[82] Olmez-Hanci, T., Arslan-Alaton, I., Dursun, D., 2014. Investigation of the toxicity of common oxidants used in advanced oxidation processes and their quenching agents. J Hazard Mater 278, 330–335. https://doi.org/10.1016/j.jhazmat.2014.06.021.

[83] Grote, M., Boudenne, J.-L., Croué, J.-P., Escher, B.I., von Gunten, U., Hahn, J., et al., 2022. Inputs of disinfection by-products to the marine environment from various industrial activities: comparison to natural production. Water Res 217, 118383. https://doi.org/10.1016/J.WATRES.2022.118383.
[84] Li, X., Chen, S., Zeng, J., Chabi, K., Song, W., Xian, X., et al., 2020. Impact of chlorination on cell activation, toxin release and degradation of cyanobacteria of development and maintenance stage. Chem Eng J 397, 125378. https://doi.org/10.1016/j.cej.2020.125378.
[85] Ebenezer, V., Nancharaiah, Y.V., Venugopalan, V.P., 2012. Chlorination-induced cellular damage and recovery in marine microalga, Chlorella salina. Chemosphere 89, 1042–1047. https://doi.org/10.1016/J.CHEMOSPHERE.2012.05.067.
[86] Olenina, I., Hajdu, S., Edler, L., Andersson, A., Wasmund, N., Busch, S., et al., 2006. Biovolumes and size-classes of phytoplankton in the Baltic Sea. HELCOM Balt Sea Environ Proc 106.
[87] Omar, N., Prášil, O., Mccain, J., Campbell, D., 2022. Diffusional interactions among marine phytoplankton and bacterioplankton: modelling H2O2 as a case study. Microorganisms 10, 821. https://doi.org/10.3390/MICROORGANISMS10040821.
[88] Yokote, M., Honjo, T., Asakawa, M., 1985. Histochemical demonstration of a glycocalyx on the cell surface of Heterosigma akashiwo. Mar Biol 88, 295–299. https://doi.org/10.1007/BF00392590.
[89] Cho, K., Ueno, M., Liang, Y., Kim, D., Oda, T., 2022. Generation of reactive oxygen species (roS) by harmful algal bloom (HAB)-forming phytoplankton and their potential impact on surrounding living organisms. Antioxidants 11. https://doi.org/10.3390/antiox11020206.
[90] Dorantes-Aranda, J.J., Seger, A., Mardones, J.I., Nichols, P.D., Hallegraeff, G.M., 2015. Progress in understanding algal bloom-mediated fish kills: The role of superoxide radicals, phycotoxins and fatty acids. PLoS One 10, 1–26. https://doi.org/10.1371/journal.pone.0133549.
[91] Burson, A., Matthijs, H.C.P., de Bruijne, W., Talens, R., Hoogenboom, R., Gerssen, A., et al., 2014. Termination of a toxic Alexandrium bloom with hydrogen peroxide. Harmful Algae 31, 125–135. https://doi.org/10.1016/J.HAL.2013.10.017.
[92] Almuhtaram, H., Hofmann, R., 2022. Evaluation of ultraviolet/peracetic acid to degrade M. aeruginosa and microcystins -LR and -RR. J Hazard Mater 424, 127357. https://doi.org/10.1016/J.JHAZMAT.2021.127357.
[93] Munoz, M., Cirés, S., de Pedro, Z.M., Colina, J.Á., Velásquez-Figueroa, Y., Carmona-Jiménez, J., et al., 2021. 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, 143197. https://doi.org/10.1016/j.scitotenv.2020.143197.
[94] Gao, L., Pan, X., Zhang, D., Mu, S., Lee, D.J., Halik, U., 2015. Extracellular polymeric substances buffer against the biocidal effect of H2O2 on the bloom-forming cyanobacterium Microcystis aeruginosa. Water Res 69, 51–58. https://doi.org/10.1016/J.WATRES.2014.10.060.
[95] Laroche, C., 2022. Exopolysaccharides from microalgae and cyanobacteria: diversity of strains, production strategies, and applications. Mar Drugs 20, 336. https://doi.org/10.3390/MD20050336.
[96] Kim, J., Huang, C.H., 2021. Reactivity of peracetic acid with organic compounds: a critical review. ACS Environ Sci. Technol. Water 1, 15–33. https://doi.org/10.1021/ACSESTWATER.0C00029/ASSET/IMAGES/MEDIUM/EW0C00029_0020.GIF.
[97] Leunert, F., Eckert, W., Paul, A., Gerhardt, V., Grossart, H.P., 2014. Phytoplankton response to UV-generated hydrogen peroxide from natural organic matter. J Plankton Res 36, 185–197. https://doi.org/10.1093/PLANKT/FBT096.
[98] Pedersen, L.-F., Rojas-Tirado, P., Arvin, E., Pedersen, P.B., 2019. Assessment of microbial activity in water based on hydrogen peroxide decomposition rates. Aquac Eng 85, 9–14. https://doi.org/10.1016/J.AQUAENG.2019.01.001.
[99] Twiner, M.J., Dixon, S.J., Trick, C.G., 2001. Toxic effects of Heterosigma akashiwo do not appear to be mediated by hydrogen peroxide. Limnol Oceanogr 46, 1400–1405. https://doi.org/10.4319/lo.2001.46.6.1400.
[100] Twiner, M.J., Trick, C.G., 2000. Possible physiological mechanisms for production of hydrogen peroxide by the ichthyotoxic flagellate Heterosigma akashiwo. J Plankton Res 22, 1961–1975. https://doi.org/10.1093/plankt/22.10.1961.
[101] von Gunten, U., 2018. Oxidation processes in water treatment: are we on track. Environ Sci Technol 52, 5062–5075. https://doi.org/10.1021/acs.est.8b00586.
[102] Shah, A.D., Liu, Z.Q., Salhi, E., Höfer, T., Von Gunten, U., 2015. Peracetic acid oxidation of saline waters in the absence and presence of H2O2: secondary oxidant and disinfection byproduct formation. Environ Sci Technol 49, 1698–1705. https://doi.org/10.1021/es503920n.
[103] Domínguez Henao, L., Turolla, A., Antonelli, M., 2018. Disinfection by-products formation and ecotoxicological effects of effluents treated with peracetic acid: a review. Chemosphere 213, 25–40. https://doi.org/10.1016/j.chemosphere.2018.09.005.
[104] Chen, T., Wang, R., Zhang, A., Xu, T., Xiao, R., Chu, W., et al., 2020. Peroxymonosulfate/chloride disinfection versus sodium hypochlorite disinfection in terms of the formation and estimated cytotoxicity of CX3R-type disinfection by-products under the same dose of free chlorine. Chem Eng J, 123557. https://doi.org/10.1016/j.cej.2019.123557.
[105] Schreck, A., Knorr, A., Wehrstedt, K.D., Wandrey, P.A., Gmeinwieser, T., Steinbach, J., 2004. Investigation of the explosive hazard of mixtures containing hydrogen peroxide and different alcohols. J Hazard Mater 108, 1–7. https://doi.org/10.1016/J.JHAZMAT.2004.01.003.
[106] Lu, X., Shao, Y., Gao, N., Chen, J., Deng, H., Chu, W., et al., 2018. Investigation of clofibric acid removal by UV/persulfate and UV/chlorine processes: kinetics and formation of disinfection byproducts during subsequent chlor(am)ination. Chem Eng J 331, 364–371. https://doi.org/10.1016/j.cej.2017.08.117.
[107] Rodríguez-Chueca, J., Giannakis, S., Marjanovic, M., Kohantorabi, M., Gholami, M.R., Grandjean, D., et al., 2019. Solar-assisted bacterial disinfection and removal of contaminants of emerging concern by Fe2+-activated HSO5- vs. S2O82- in drinking water. Appl Catal B Environ 248, 62–72. https://doi.org/10.1016/J.APCATB.2019.02.018.
[108] Dock, A., Linders, J., David, M., Gollasch, S., David, J., 2019. Is human health sufficiently protected from chemicals discharged with treated ballast water from vessels worldwide? – A decadal perspective and risk assessment. Chemosphere 235, 194–204. https://doi.org/10.1016/J.CHEMOSPHERE.2019.06.101.