Innovative method of utilising hydrogen peroxide for source water management of cyanobacteria

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Received: 26 July 2021 / Accepted: 9 November 2021 / Published online: 18 November 2021
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Abstract
The treatment and control of cyanobacterial blooms using copper-based algaecides in water reservoirs have historically been used; however, due to the adverse impact of copper on the environment, water authorities have been researching and studying new and innovative ways to control cyanobacterial blooms. Hydrogen peroxide has been investigated as an environmentally friendly alternative, and this research aims to determine the impact of water quality on its effectiveness based on the decay characteristics in different water samples. Natural water samples from South Australian reservoirs and river were used to evaluate hydrogen peroxide decomposition and provide a better strategy for water operators in using it as an algaecide. Our experiments show the dependency of hydrogen peroxide decomposition not only on water quality but also on the initial hydrogen peroxide dose. A higher initial hydrogen peroxide dose can trigger the increase of pH, leading to increased consumption of hydrogen peroxide. In addition, the hydrogen peroxide decomposition is significantly accelerated with the rise of copper concentration in water samples. Moreover, it is found that UV light can also affect the decomposition rate of hydrogen peroxide. The hydrogen peroxide decay is more significant under UV light for the samples with lower hydrogen peroxide concentrations. Our study also shows the impact of dissolved organic carbon (DOC) on hydrogen peroxide decomposition is not substantial. The study also presents a modelling method to optimise hydrogen peroxide application based on water quality characteristics. Our findings can provide knowledge for the water industry to produce a suitable model which can be used to optimise the application of hydrogen peroxide for the control of cyanobacteria.

Keywords Algal blooms · Algaecides · Copper sulphate · Hydrogen peroxide · Decomposition

Introduction
Population increase, urban growth and expansion of agricultural practices have led to the increase of nutrient levels in the environment and waterways (Newcombe et al. 2012). This increase in nutrient concentration and increase in global temperatures, due to the climate change (Jančula & Maršálek 2011, Newcombe et al. 2012), have had an obvious negative impact on the aquatic ecosystem, especially in the mass development of cyanobacteria in water resources (Jančula & Maršálek 2011). Cyanobacteria are well known for toxin production, and their presence in waterways has been the focus of many studies over recent decades given the environmental and health risks they pose on humans and other living species, such as livestock, wild mammals, birds and fishes (Dreyfus et al. 2016, García-Villada et al. 2004, Stewart et al. 2008). A variety of compounds produced by cyanobacteria have implications for human health including hepatotoxic peptides, neurotoxic cyclic alkaloids, multitarget alkaloids and skin irritant lipopolysaccharides (Yunes 2019). Humans can suffer from heart and kidney diseases, gastrointestinal irritation, liver failure or even death due to consumption of these toxins (Carmichael & Boyer 2016, Fitzgerald et al. 1999; He et al. 2012; Westrick et al. 2010). This highlights the importance of having access to high quality and...
appropriately treated drinking water (Antoniou et al. 2013; Chow et al. 1999; Westrick et al. 2010; Xing et al. 2015). Moreover, cyanobacteria pose a challenge for water supply systems due to production of unpleasant taste and odour compounds (García-Villada et al. 2004, Lee et al. 2017). Consequently, this requires a more intensive and costly treatment process to eliminate their presence (Hitzfeld et al. 2000).

To improve the effectiveness of treatment, a variety of options have been proposed to control cyanobacteria in the source waters. Stroom and Kardinaal (2016) identified two major approaches to removing cyanobacteria, namely preventative and control. Preventative measures involve improvement of the chemical and biological health of the system and control encompasses direct actions to stop cyanobacteria proliferation. In reservoirs, one such direct control is chemical treatment using algaecides which have been widely utilised and extensively studied as a way of reducing cyanobacteria numbers prior to conventional drinking water processing (Antoniou et al. 2013; Chow et al. 1994; Fan et al. 2014, García-Villada et al. 2004). This includes the use of copper sulphate, copper chelates, aluminium sulphate or potassium permanganate algaecides (Fan et al. 2014, García-Villada et al. 2004). Amongst these algaecides, the toxicity of copper sulphate on cyanobacteria cells and its effectiveness of algae elimination and cell density control have been widely studied and documented (Costas & López-Rodas 2006, Fan et al. 2013, García-Villada et al. 2004). Using copper sulphate is also economical and relatively safe for human health as well as easy to apply (Fan et al. 2013, García-Villada et al. 2004, Jančula & Maršálek 2011). Copper sulphate is generally applied at the early stage of bloom formation. However, this treatment does not totally remove all cyanobacteria, and repeat doses are required when cyanobacteria once again return (García-Villada et al. 2004). Furthermore, it has been speculated that the excessive treatment of algae, using copper sulphate, can develop cell resistance, which requires higher concentration and more frequent treatments (García-Villada et al. 2004, Kansole & Lin 2017, Murray-Gulde et al. 2002). The excessive use of copper sulphate can also impact on the biotic and abiotic fresh water characteristics (Song & Wang 2015) and has a serious ecological impact on non-target species (Greenfield et al. 2014, Jančula & Maršálek 2011). For example, copper has a toxic effect on aquatic organisms including crustaceans, daphniids, and fish, Danio rerio (Closson & Paul 2014, Jančula & Maršálek 2011, Murray-Gulde et al. 2002). Additionally, copper can be transported from the water supply reservoir in a dissolved organic or inorganic form raising the risk of metal accumulation and toxicity in sediments (Fan et al. 2013, Jančula & Maršálek 2011). The excessive and incorrect use of copper sulphate dosing has also been associated with hepatitis illness of children and adults in Palm Island in Queensland (Kansole & Lin 2017, Prociv 2004).

Many researchers have shown hydrogen peroxide (H₂O₂) as a viable replacement for copper-based algaecides in terms of its availability, cost and selectivity towards cyanobacteria over other more desired green algae (Drábková et al. 2007, Matthijs et al. 2012, Sukenik & Kaplan 2021, Weenink et al. 2015). The use of hydrogen peroxide in place of copper-based algaecides also removes the long-term issue of heavy metal contamination of ecosystems. While there has been extensive assessment of efficacy of hydrogen peroxide as an algaecide, there is very little research on the impact of different water types with various chemical characteristics on residual H₂O₂. This relationship between hydrogen peroxide and water chemistry will be important in determining the dose level for a particular water body. The current paper presents results from an investigation of the effects of different water chemistries on H₂O₂ decomposition and development of a models to estimate the H₂O₂ decomposition in water over time. This information will be valuable in understanding the activity of H₂O₂ as an algaecide in natural waters and help operators develop its use to control cyanobacterial blooms.

**Materials and methods**

**Site selection and sample collection**

Experimental waters were sourced from three South Australian locations that have had a history of cyanobacterial blooms and include Happy Valley Reservoir, Torrens River and Myponga Reservoir. Happy Valley Reservoir is located in Adelaide and supplies drinking water to over half a million people. The Torrens River is a recreational water course located near Adelaide’s CBD. Myponga Reservoir is located about 60 km south of Adelaide, and it is fed by the Myponga River and other smaller catchment streams and provides about 5% of Adelaide’s water supply.

Samples collected from these three sites were filtered through a 90-mm glass microfiber filter GF/C and kept in a refrigerator under 4 °C. All glassware and storage containers were washed three times with distilled water, followed by three washes with ultrapure deionised water (Milli-Q element, 18.2 MΩ) before a final rinse with the reservoir water used in each experiment.

**Materials, reagents and solutions**

Sodium percarbonate (SP) stock solution was prepared by dissolving 18.382 g granulated SP (IXOM Operations Pty Ltd) in 1 L of Milli-Q water to give a final hydrogen
peroxide concentration of 5 g/L. This stock solution was used to simulate the same method of \( \text{H}_2\text{O}_2 \) dosing in reservoir water. Copper sulphate solution was prepared by dissolving 9.82 g of \( \text{CuSO}_4.5\text{H}_2\text{O} \) (AR, Chem-Supply) in 1 L of Milli-Q water. Buffer stock to perform the \( \text{H}_2\text{O}_2 \) concentration measurement was prepared by mixing 18 mL of 0.5 mol/L \( \text{Na}_2\text{HPO}_4 \) and 82 mL of 0.5 mol/L \( \text{NaH}_2\text{PO}_4 \) to achieve pH 6 in tested samples. N,N-diethyl-1,4-phenlenediammonium sulphate (DPD) reagent was prepared by diluting 0.1 g of N,N-diethyl-1,4-phenlenediammonium sulphate, Fluka, in 10 mL of 0.1 N \( \text{H}_2\text{SO}_4 \). Horseradish peroxidase reagent was prepared by diluting 10 mg of horseradish peroxidase, Type II, 181 purpurogallin units/mg, in 10 mL of Milli-Q water (Drábková et al. 2007).

### \( \text{H}_2\text{O}_2 \) analysis/concentration determination

The method used to measure the \( \text{H}_2\text{O}_2 \) concentration was adapted from Drábková et al. (2007), which was modified from Bader et al. (1988). Thirty percent \( \text{H}_2\text{O}_2 \) solution (AR, Chem-Supply) was used to create \( \text{H}_2\text{O}_2 \) standard solutions. Two \( \text{H}_2\text{O}_2 \) standard curves were prepared to determine the \( \text{H}_2\text{O}_2 \) at low and high concentrations. The standard curve to determine low \( \text{H}_2\text{O}_2 \) concentration of less than 5 mg/L \((0, 0.056, 0.113, 0.226, 0.564, 1.13 \text{ and } 5.64 \text{ mg/L})\) was prepared by mixing 16.6 \( \mu \text{L} \) of \( \text{H}_2\text{O}_2 \) standard solution to 1 L of Milli-Q water, followed by multiple dilutions. The standard curve to measure high \( \text{H}_2\text{O}_2 \) concentration of more than 5 mg/L \((0, 0.11, 0.57, 1.13, 2.27, 3.4, 6.8 \text{ and } 13.6 \text{ mg/L})\) was prepared by mixing 1 mL of \( \text{H}_2\text{O}_2 \) to 1 L of Milli-Q water, then followed by multiple dilutions. Standard solutions were then analysed in Agilent Cary 60 UV–Vis spectrophotometer at 551.0 nm.

For \( \text{H}_2\text{O}_2 \) concentrations up to 5 mg/L, 100 \( \mu \text{L} \) of the buffer solution, 50 \( \mu \text{L} \) of DPD reagent and 50 \( \mu \text{L} \) of HRP reagent and 900 \( \mu \text{L} \) of the water sample were mixed in a polystyrene cuvette by inverting before immediately placing in UV–VIS spectrophotometer and measuring absorbance. Concentration was then determined from the corresponding standard curve. For \( \text{H}_2\text{O}_2 \) concentration greater than 5 mg/L, 100 \( \mu \text{L} \) of the buffer solution, 850 \( \mu \text{L} \) of Milli-Q water, 50 \( \mu \text{L} \) of DPD reagent and 50 \( \mu \text{L} \) of HRP reagent were used. All measurements were made in triplicate.

### Investigate the effects of different parameters on \( \text{H}_2\text{O}_2 \) decomposition

a. The effects of different water types

A 200 mL volume of either Milli-Q water or experimental water samples was dosed with 40, 200, 400 and 800 \( \mu \text{L} \) of SP solution to achieve initial concentrations of 1, 5, 10 and 20 mg/L \( \text{H}_2\text{O}_2 \). All samples were incubated (Thermoline Scientific TRIL-1175–2-SD) at 20 °C in the dark over a 24-h period to ensure the change in \( \text{H}_2\text{O}_2 \) concentration was not affected by changes in light or temperature. The water samples were collected at the time of initial dosage, and on every hour for a period of 7 h to determine the \( \text{H}_2\text{O}_2 \) concentrations. At the same time, pH was measured using Oakton pH Meter (510 series) every hour for each water sample across all the four concentrations. Additionally, the \( \text{H}_2\text{O}_2 \) level was again measured 24 h later from the initial dosage.

b. Additional control experiments

i. The effect of UV light

The experiment was conducted in Happy Valley reservoir water using the same method, concentrations and conditions as presented in Sect. 2.4a except in the presence of UV light. All samples were kept in the incubator under two UV lamps (Dermfix 3000 phototherapy 310–312 nm spectrum). \( \text{H}_2\text{O}_2 \) concentrations were measured at the time of initial dosage and on every hour for a period of 7 h, with a final sample taken 24 h after the initial dosage. pH was also determined over the same period.

ii. The effect of copper sulphate under dark condition

The experiment was carried out in Milli-Q water using the same methodology presented in Sect. 2.4a but replacing hydrogen peroxide with 0.5 mg/L \( \text{Cu}^{2+} \). pH was determined as described previously.

iii. The effect of DOC under dark condition

The experiment was carried out in Milli-Q water as described in Sect. 2.4a but with inclusion of dissolved organic carbon (DOC) extract as surrogate of natural organic matter (NOM) present in natural water samples. The DOC was added to the samples using the laboratory organic extract adopted from the Spent Brine of Mt Pleasant, South Australia, MIEX based Water Treatment Plant. Two hundred microlitres of the organic compound was dosed into 200 mL samples to achieve 10 mg/L DOC in all samples. \( \text{H}_2\text{O}_2 \) concentrations and pH were also determined using the same procedure as previously described.

### Data analysis and model development

Experimental data was initially processed and analysed using Microsoft Excel. For further data analysis and model
assessment, the three-column $\text{H}_2\text{O}_2$ concentration, dosage and time data were further analysed using TableCurve3D, Systat Software, Inc., to obtain the equation of best fit. TableCurve3D used the built-in equation types/equations to fit the experimental data and ranked against the $r^2$ value. The simple equation option was initially selected; if $r^2$ values were good, > 0.95, then simple equation will be used to provide the best equation for the decay characteristic of each water sample, which were then used to establish an initial prediction model. By using the coefficients which were determined by the fitting procedure, the $\text{H}_2\text{O}_2$ decay behaviour can be established for each water source; thus, the CT (contact time $\times$ concentration) value can be determined.

**Results and discussion**

**Characteristic of water sources**

The filtered water samples from three field sites were analysed to determine chemical characteristics. The results in Table 1 show that the total iron concentrations in filtered water samples were between 0.11 and 0.21 mg/L, TKN was between 0.69 and 0.97 mg/L and pH between 7.6 and 8 from three field sites. Torrens River and Happy Valley have similar total manganese levels of approximately 0.045 mg/L which is much higher than Myponga, with only 0.002 mg/L. Happy Valley has the lowest total phosphorus concentrations compared to others.

However, total copper and DOC concentrations showed large differences amongst the samples; Happy Valley water had a significantly higher total copper level compared to Torrens River (136 times higher) and Myponga Reservoir (17 times higher). Myponga Reservoir water had the highest DOC level of 13.8 mg/L amongst the three water sources (Table 1). The rest of study will be concentrating on the impact of copper and DOC on $\text{H}_2\text{O}_2$ decomposition.

**The effects of different water types on $\text{H}_2\text{O}_2$ decomposition**

Figure 1 shows the effect of $\text{H}_2\text{O}_2$ dosages on pH. Two trends, low doses (1 mg/L and 5 mg/L) and high doses (10 mg/L and 20 mg/L), were observed. For low $\text{H}_2\text{O}_2$ dosages, an observable trend of pH decreased slightly after the addition of $\text{H}_2\text{O}_2$ then increased after 24 h in the field water samples. For high dosages, pH initially increased then

| Table 1 Measured water quality parameters for water samples collected from three field sites |
|-------------------------------------------|
| pH | Torrens River | Myponga | Happy Valley |
|----|--------------|---------|--------------|
|    | 8.0          | 7.6     | 7.9          |
| Iron—total (mg/L) | 0.108 | 0.208 | 0.196 |
| Manganese—total (mg/L) | 0.045 | 0.002 | 0.049 |
| Phosphorus—total (mg/L) | 0.036 | 0.035 | <0.003 |
| TKN (mg/L) | 0.97 | 0.83 | 0.69 |
| Copper—total (mg/L) | 0.003 | 0.025 | 0.435 |
| DOC (mg/L) | 5.9 | 13.8 | 7.1 |

Note: TKN total Kjeldahl nitrogen

**Fig. 1** pH changes in the water samples at different dosages, 1 mg/L, 5 mg/L, 10 mg/L and 20 mg/L, of $\text{H}_2\text{O}_2$ over 24 h in a) Milli-Q, b) Torrens River, c) Myponga and d) Happy Valley.
decreased after 24 h. There is also another general trend of pH increase with the increasing H₂O₂ concentration. Milli-Q water has the highest pH increase (to pH 10) after addition of H₂O₂ compared to the field water samples (increased to about pH 9); the final high pH in Milli-Q after addition of H₂O₂ is likely caused by the low buffering capacity of Milli-Q water. For the Myponga samples and Milli-Q water with low doses of H₂O₂, pH remained relatively constant over 24 h after addition of H₂O₂. The initial increase in pH after high H₂O₂ may explain the initial rapid loss of H₂O₂ concentration in high-dose situations (will be discussed in the following sections).

Figure 2 presents the H₂O₂ decomposition (decay) for different water types over 24 h. Our results show that there is no observable change in H₂O₂ concentration (decomposition) in Milli-Q water at different concentrations after 24 h compared to other water types for low H₂O₂ concentration (1 mg/L). However, for high doses, a rapid initial drop in H₂O₂ concentration is observed (all four water types); this could be related to the initial increase in pH after H₂O₂ addition reported earlier. Torrens River samples showed a slow decomposition of H₂O₂. The H₂O₂ concentration decreased by 41%, 30%, 33% and 33% of the initial H₂O₂ concentrations of 1, 5, 10 and 20 mg/L, respectively after 24 h. The results of Myponga Reservoir water samples presented a similar trend compared to Torrens water. The H₂O₂ concentrations in the samples reduced by 23%, 22%, 24% and 22% compared to initial concentrations of 1, 5, 10 and 20 mg/L, respectively. Conversely, the results of Happy Valley water samples showed a significant variation in H₂O₂ decomposition over the 24-h period across all four concentrations. The results shown in Fig. 1 demonstrate a significant drop in the concentration with 100% loss of H₂O₂ at high H₂O₂ dosages (10 and 20 mg/L), 95% was lost at 5 mg/L dosage, while 67% was lost at 1 mg/L dosage after 24 h. The results also showed a rapid decomposition in the early stage for the Happy Valley water samples where 24% was decomposed at 1 mg/L, 45% at 5 mg/L, 72% at 10 mg/L and 81% at 20 mg/L after the first hour. In general, for all water samples, the percentage lost has a direct relationship with the H₂O₂ dose, i.e. the higher the H₂O₂ dose the higher the percentage reduction. Studies showed that H₂O₂ was more stable in low and moderate pH. However, when the pH continued to increase and reached alkalinity condition, it could lead to high consumption of H₂O₂ in solutions (Lee et al. 2013; Pędziwiatr 2018, Yazici & Deveci 2010). From Fig. 1, we can see that higher initial dose of H₂O₂ triggered a significant change of pH after H₂O₂ was added. The increased pH can result into a rising rate of reaction for H₂O₂, leading to higher percentage reduction of H₂O₂ (Fig. 2). From this result, higher H₂O₂ dose does not necessarily mean the H₂O₂ will perform better than lower H₂O₂ dose. If the system’s pH increases significantly after initial dose of H₂O₂, it could cause rapid consumption of H₂O₂, affecting its performance as an algaecide. In addition, over-application of H₂O₂ is not economic for the water authorities.

Furthermore, Happy Valley water showed a substantial and rapid loss of H₂O₂ concentration across all samples in comparison to Torrens River and Myponga Reservoir water. It was reported that the amount of copper was much higher in Happy Valley compared to Torrens River and Myponga Reservoir water, and it is assumed that this is the reason for high H₂O₂ decomposition in Happy Valley water. To confirm whether the metal contents influenced the results, as
The results of adding copper sulphate to the Milli-Q water test solutions showed a slower reduction with only 42% of $\text{H}_2\text{O}_2$ loss after 24 h, while the 5 mg/L $\text{H}_2\text{O}_2$ samples showed a 97% loss after the same duration. The samples with both 10 and 20 mg/L $\text{H}_2\text{O}_2$ (high dosages) showed a rapid loss of $\text{H}_2\text{O}_2$ with 100% removal after 24 h.

The results of the Milli-Q water mixed with similar copper concentration found in Happy Valley water samples of 0.5 mg/L showed very similar behaviour to the $\text{H}_2\text{O}_2$ decomposition of the Happy Valley water experiment conducted in the dark. This was in complete contrast to the Milli-Q water alone. These results suggest the rapid decay observed in the Happy Valley water samples was due to the presence of copper in the reservoir water. These results are consistent with the study of Akagawa and Suyama (2002), which indicated that $\text{Cu}^{2+}$ was more effective than $\text{Fe}^{3+}$ in catalysing the $\text{H}_2\text{O}_2$ and could generate hydroxyl radicals at a much higher rate than $\text{Fe}^{3+}$. Others studies from Yazici and Deveci (2010) and Mlasi (2015) of $\text{H}_2\text{O}_2$ decomposition in the presence of copper also confirmed that the copper acts as a catalyst, which could accelerate $\text{H}_2\text{O}_2$ decay. Yazici and Deveci (2010) and Mlasi (2015) showed the $\text{H}_2\text{O}_2$ decomposition was also significantly accelerated as the amount of copper was increased. In addition, Lee et al. (2013) indicated that the catalytic decomposition of $\text{H}_2\text{O}_2$ by $\text{Cu}^{2+}$ could be accelerated when pH increased. This is because the deprotonated form of $\text{H}_2\text{O}_2$ could act as the major electron donor for the reduction of $\text{Cu}^{2+}$. Therefore, the pH increase in solutions caused by higher initial $\text{H}_2\text{O}_2$ dose can also accelerate $\text{H}_2\text{O}_2$ decay under the presence of $\text{Cu}^{2+}$.

Based on the experimental results, it has been confirmed that $\text{H}_2\text{O}_2$ decomposition is dependent on water quality, especially the amount of metals present. It was also confirmed that water types consisting of low metal contents, such as Torrens River and Myponga Reservoir water, can maintain $\text{H}_2\text{O}_2$ residual for over a 24-h period. However, if metal content is high, such as observed in the Happy Valley samples, the algicidal activity of $\text{H}_2\text{O}_2$ could be impacted. In addition, the pH changes after the initial doses of $\text{H}_2\text{O}_2$ could further affect the $\text{H}_2\text{O}_2$ decomposition with the presence of metals (Lee et al. 2013). Therefore, determining the optimum initial dose of $\text{H}_2\text{O}_2$ in the water bodies under laboratory condition is recommended before any large-scale application of $\text{H}_2\text{O}_2$ in the natural waters.

The effect of UV light on $\text{H}_2\text{O}_2$ decomposition

$\text{H}_2\text{O}_2$ combined in the presence of UV light, to simulate a real algicide application in the presence of sunlight, for same sample conditions showed an increased decomposition rate compared to samples tested in the dark. One hundred percent of the initial $\text{H}_2\text{O}_2$ concentration was decomposed in the higher concentration samples of 10 and 20 mg/L in an 8- and 4-h period, respectively. This is compared to 24 and 6 h of total $\text{H}_2\text{O}_2$ lost in the dark for the same concentration.
In addition, the loss of the H$_2$O$_2$ in the first hour was greater than samples in the dark for 10 and 20 mg/L concentrations. The H$_2$O$_2$ was also 100% decomposed in all H$_2$O$_2$ doses after a 24-h period. This showed a higher decomposition rate in comparison to the same water samples and concentrations when incubated in the dark. In Fig. 4, the side-by-side comparison of H$_2$O$_2$ decomposition in the dark and in the presence of UV light, it is clearer in the low dose cases that the decay curve for samples in the dark has a higher corresponding H$_2$O$_2$ concentration than those with UV light.

Additionally, when H$_2$O$_2$ was combined with UV under the same conditions and concentrations, it was found that UV light affected the decomposition rate. This was especially evident with lower concentration samples, which maintained higher H$_2$O$_2$ residuals after a 24-h period compared to the same water tested in the dark. These results are consistent with the study of Drábková et al. (2007), which proved that low concentrations of H$_2$O$_2$ of 0.6 and 2.5 mg/L were decomposed in 3 h of exposure to UV light. Drábková et al. (2007) argued that this proved the effect of UV on improving H$_2$O$_2$ toxicity. This was explained by the rapid decomposition in the presence of UV, which produced more hydroxyl radicals and enhanced the H$_2$O$_2$ toxicity on cyanobacteria cells.

**The effect of DOC on H$_2$O$_2$ decomposition**

To understand the impact of NOM, the higher DOC concentration on H$_2$O$_2$ decomposition in Myponga Reservoir water (highest DOC concentration compared with the other samples), further experiments were conducted using Milli-Q water at similar concentration of the DOC found in Myponga Reservoir water. The Milli-Q water samples with added DOC did not show a significant loss of H$_2$O$_2$ after 24 h, a similar result to Milli-Q water without added DOC concentrations when incubated in the dark (Fig. 5).

The results shown in Fig. 5 were in line with the study of Bissey et al. (2006), which found the same decomposition rate of H$_2$O$_2$ in natural soils with organic carbon content of 1.6% and 0.2%. Huling et al. (2001) also confirmed that the decomposition of H$_2$O$_2$ was independent from organic matter, and the decomposition occurs by catalytic reaction with metals rather than the organic component. However, Autin et al. (2013) explained that DOC can compete with cyanobacteria cells to react with the hydroxyl radicals produced by H$_2$O$_2$ decay. While the current study showed no impact of DOC on H$_2$O$_2$ decay, the interaction of DOC with H$_2$O$_2$ in the presence of algal cells will need further investigation to understand any changes in algicidal activity in natural waters.

**Using curve fitting technique to model decay in the presence of copper**

From our findings, the cause of decay was mainly due to the presence of copper in the water. In this section, a curve fitting technique was applied to understand the decay behaviour of H$_2$O$_2$ in the presence of copper. The copper concentrations of Torrens River, Myponga Reservoir and Happy Valley water samples determined by copper analysis showed...
the results are in the order of magnitude difference of μg/L, 10 μg/L and 100 μg/L range, respectively. The autofit function in TableCurve3D was used to get the best fit equation, i.e. highest $r^2$ value. As explained earlier in the Materials and methods, TableCurve3D used its equation library to find the best fit equations and ranked them based on the $r^2$ value from high to low. For the Happy Valley water decay data, the top ranked equation is Eq. 302.461.513. This is the equation identification number used by the TableCurve3D software as the top ranked equation, and the equation is $z^{-1} = a + bx + c/y$, $r^2 = 0.97$, $z$ is H$_2$O$_2$ concentration in mg/L, $x$ is time and $y$ is H$_2$O$_2$ dose. The same fitting procedure was conducted for Myponga and Torrens River decay data sets. Equation 15.123.288:1 $\ln z = a + b \cdot e^{-x} + c \ln y$ is the top ranked equation for both waters, $r^2 = 1.00$ and 0.99 for Myponga and Torrens River waters, respectively. Despite the order of magnitude difference for Happy Valley, Myponga and Torrens River, the same equation/equation family was listed as the best fit for the decay curves for Torrens River and Myponga, while Happy Valley has a different equation. This indicates that the impact of copper on H$_2$O$_2$ decay may only occur when a threshold level is reached. Both the copper concentrations in Myponga (0.025 mg/L Cu) and Torrens (0.003 mg/L Cu) would be below the threshold level; thus, the same best fit equation was found to represent the decay characteristics. While in Happy Valley, the copper concentration is in 100 μg/L range, and a different equation was found to represent the decay characteristics.

Additionally, the coefficients, $a$, $b$, $c$ values, presented in Table 2 can be used determine the H$_2$O$_2$ concentration for a particular dose at a particular time to estimate the efficiency. The equation developed by this research can be used as a model to estimate the required initial H$_2$O$_2$ dose for a set contact time in a particular water type. Furthermore, a concentration and contact time (CT) value can also be determined to estimate the effectiveness of the treatment; generally longer contact time is needed for lower concentration to achieve the same effectiveness.

**Conclusion**

Cyanobacteria is an ongoing problem in water reservoirs, wastewater systems and recreational waters in South Australia (Baker & Humpage 1994). During the period of late 1990s until 2011, Torrens River was closed for some time.

| Equations for curve fitting | Happy Valley | Myponga | Torrens River |
|-----------------------------|-------------|---------|---------------|
| $z^{-1} = a + bx + c/y$     | 0.97        |         |               |
| $\ln z = a + b \cdot e^{-x} + c \ln y$ | 1.00        | $a = 0.296, b = 0.177, c = 1.020$ |
| $\ln z = a + b \cdot e^{-x} + c \ln y$ | 0.99        | $a = 0.355, b = 0.267, c = 0.998$ |
during summer periods because of algae growth, which formed scums, produced unpleasant odours and released toxins that could impact both the human and the natural environment. Copper sulphate has been used in South Australia for more than 50 years to control algal growth in some of the state’s reservoirs. However, its harmful impact on the environment and increasing cost of the chemical have driven our local water utility, SA Water, to identify and develop innovative alternative algal control methods. One of the potential alternatives, sodium percarbonate, is considered a more environmentally friendly option than copper sulphate. This study investigated hydrogen peroxide decomposition in different natural water samples from South Australia, including two reservoirs and a river, to provide a better understanding of its activity as an algaecide. The results from our research have shown that water quality and chemistry can play an important role in hydrogen peroxide decomposition in water and in turn its toxicity to cyanobacteria. It is evident that water components, especially metals, such as ambient level of copper in the reservoir, can impact the rate of decomposition of H₂O₂ in natural waters. Additionally, the pH changes related to the initial H₂O₂ does can affect the rate of decomposition of H₂O₂ in water. Moreover, this work highlights the effect of UV light availability on the decomposition of H₂O₂. The knowledge gained from this research will be important for constructing a model explaining the interactions of hydrogen peroxide in natural systems and developing formulae to help reservoir operators determine the required algaecide dose for removal of problem cyanobacteria.

Acknowledgements The authors would like to thank UniSA STEM and SA Water to support Maximus Ghaly’s Master study.

Author contribution JH: experimental design, data analysis, manuscript writing, and supervision. MG: experiment, data analysis, and manuscript writing. PH: experimental design, manuscript writing, and supervision. CWKC: experimental design, data analysis, manuscript writing, and supervision.

Data Availability Not applicable.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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