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Mathematical simulation to up-scale electrolysis for effective suppression of freshwater cyanobacteria

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ABSTRACT

Electrolysis, originally applied for removal of various pollutants from water and wastewater, has been recently found to be successful in the suppression and removal of cyanobacteria in freshwaters. Existing studies addressed crucial operational parameters based on batch laboratory studies; however, only very few studies have projected this information for continuous process to up-scale for industrial application. Oxygen Productive Electrode (OPE), a new type of electrolysis unit, is recommended as pre-treatment of freshwaters polluted by cyanobacterial blooms prior to conventional water treatment process. In this study, the data on suppression rate of *Aphanizomenon* sp., a filamentous cyanobacteria, from prior experimental work were used to mathematically evaluate the effects of configuration of OPEs as a pre-treatment stage of a water treatment plant. As it was found, the single-stage batch OPE was observed to be less effective on filamentous cyanobacteria than on coccus and unicellular cyanobacteria, thus an engineering consideration was made to improve system efficiency by estimating the overall system efficiency when multiple OPEs were implemented in series in continuous operation at steady state.

Keywords: Filamentous; Cyanobacteria; Electrolysis; Freshwaters; Industry; OPEs in series

1. Introduction

Electrolysis has been used worldwide in water and wastewater treatment to remove various pollutants including nutrients, COD, phenols, dyes, petroleum refinery wastewaters, pesticides, leachates and persistent organic pollutants, which are endocrine disrupting chemicals [1–6]. However, lesser number of studies has focussed on removal of nuisance or harmful algae, typically cyanobacteria, with this technology.

There were, however, a few reports published on application of electrolysis on removal of cyanobacteria and its toxins in highly polluted wastewaters containing metals and vast amount of chemicals [1,3,5,6] to

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ensure sludge of low cyanobacteria or toxin content. Electrolysis has also been successfully implemented in seawater to remove algae which are contributors of ammonia and total chemical oxygen demand [4]. Mechanisms and operational factors of electrolysis differ substantially between those in wastewaters, seawaters and in freshwaters. Electrolysis for wastewater treatment is applied only after the use of biological treatment as pre-treatment to remove the high content of suspended solids [3–6]. Thus, electrolysis for wastewater and seawater treatment is also more costly than for freshwater treatment [3,4]. However, this is not the case for freshwater application where levels of suspended solids are generally much lower making it less costly. Electrolysis can be used independently without the need of any pre-treatment for freshwaters.

Even though various physical or chemical technologies including aeration and more advanced oxidation processes, such as Fenton and hydrogen peroxide, have been investigated for removal of microcystin toxins, these technologies have been found not capable of completely destroying the toxins unlike electrolysis [4–6]. This is another reason why this technology is preferred in addition to its successful suppression of *Microcystis* sp. growth [1,7].

Mechanisms of electrolysis are commonly categorized as electro-oxidation/disinfection, electro-flocculation or electro-flotation, or combination of more than one of these [1,5]. Mechanism of electrolysis system in our study is mainly electro-oxidative using solid polymer electrode and differs from previous ones in many ways [7–12]. This system is not dependent on or relevant to presence of chloride or chlorine, neither is used as precursor for the formation of oxidants unlike some systems [2,4,13]. Instead chloride is considered as an impurity that reduces the performance of the membrane-based electrolysis by poisoning anode, which leads to serious performance deterioration [7,8,9,14,15]. This electrolysis depends on oxygen-reactive species, which are mainly ozone and hydroxyl radicals rather than the production of hydrogen as species responsible in the removal of the cyanobacteria [7,8,10,11]. Hydrogen is channelled out from the device as a fuel if collected in large quantity.

Studies on electrolysis have mainly centred around mechanism [3,4,7–9,13,16–21] and characterizing operational parameters such as electrode materials [1,13,15,17,19], electrode location /point of use [1,6], nature of ionic species [2,9,14,16], production rate of species responsible [5,7,9,19,20,22], power applied [1,5,17], voltage applied/achieved [4–9,13,14,22], flow rates [1, 4], current intensities/densities [1–3,6,8,9,13,14,22], mixing speed [1], temperature [5,17,20–22], retention time [4], algal loading [1,5], stability of pH [7–9], presence of organics, alkalinity and suspended solids [3–5,16,18] for performance or removal efficiency. These are mostly laboratory batch experiments with some continuous processes and a few on wastewaters. However, there is a lack of scale-up studies from engineering point of view as highlighted by Sharma et al. [16] creating the need for such work to enable practical and sustainable application of electrolysis in water treatment plants (WTPs).

Having said so, since viable filamentous cyanobacteria are difficult to remove from water by coagulation/sedimentation, filtration and/or other physico-chemical means, it is beneficial to install oxygen productive electrode (OPE) as a pre-treatment process, prior to primary solid-liquid separator at the WTP, which is capable of suppressing (killing) filamentous cyanobacteria. It is widely known that inviable filamentous cyanobacteria are more efficiently separated from water and dewatered. This cyanobacteria could be harvested for other beneficial means for a better overall system management. OPE is an applicable system as the pre-treatment process due to its simple structure, energy-saving characteristics and, the most importantly, its environmentally friendly principle.

This study aims to provide useful information for up-scaling purpose using engineering calculations towards implementation of the data obtained by single-stage batch OPE experiments extended to multiple OPEs in series process as a pre-treatment stage in WTP where freshwater is exposed to algal blooms. Prior to this, filamentous cyanobacteria suppression rates are experimentally determined in OPE electrolysis treatment and used for this mathematical scale-up.

2. Materials and methods

2.1. Cyanobacteria suppression experiment

This experiment was conducted using electrolysis system (OPE) made of titanium base coated with platinum anode and stainless steel as cathode with Nafion® 117 (DuPont de Nemours, Wilmington, DE, USA) as the solid polymer electrode (SPE) membrane. The OPE (Fig. 1) was earlier developed by the authors and Ishizaki Company [13–18], but recently modified and re-produced for the use of this study by Seto Engineering Co Ltd (Chiba, Japan)[1]. The anode pattern used is mesh (Fig. 1) for its ability to produce higher oxygen transfer coefficient, K_La [12]. Previous OPE units were of different dimensions and made of different electrode materials [7,8–12]. The 16 mm OPE was

[1]OPE is currently available from Imaisei Sakusho Co., Ltd., Ibaraki, JAPAN.

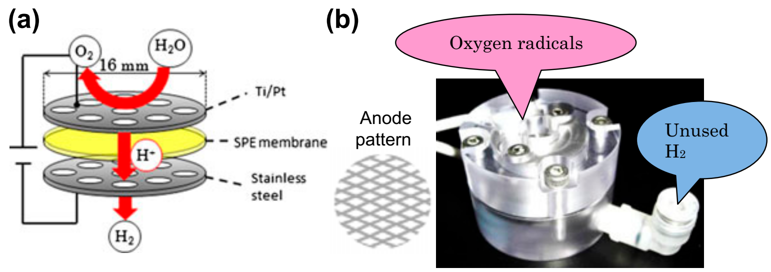

Fig. 1. Pictures of OPE shown A. OPE schematic diagram B. anode pattern (mesh) C. point where radicals are released.

operated with an optimum 0.06 A current producing a current density of 40 mA/cm^2. Meanwhile, the gas production of OPE is 0.6 ml/min and oxygen transfer coefficient (K_La) is 1.00 ± 0.16 mg/L/h at water temperature of 25 ± 2˚C. Dissolved oxygen (DO) and cyanobacterial density were determined throughout a 4 d experiment in 1.5 L volume of initial 8,000 filaments/ml cyanobacteria-spiked medium [8]. The data obtained in the experiment are used to estimate suppression rate constant of the *Aphanizomenon* sp. using trend-line data of natural log calculations of cyanobacterial density achieved every 24 h, plotted against time for the entire 4 d experiment.

2.2. Mathematical evaluation

The estimated cyanobacterial suppression rate of the batch experiment in Section 2.1 was then applied to continuous-flow stirred-tank reactor model for considering desirable configuration and specifications for actual implementation. In order to obtain best system performance with regard to cyanobacterial suppression, comparisons were made for single and multiple OPEs in series. For the multiple OPEs in series configuration, the system with two, five and 10 OPEs connected in series were considered. Overall hydraulic retention times (HRT) investigated were up to a maximum of 7 d. A simple mass balance equation was established for the OPE unit and simplified by assuming complete mixing and steady state.

3. Results and discussion

3.1. Mathematical expression

The *Aphanizomenon* sp. cyanobacteria suppression experiment (Section 2.1) provided a net suppression rate value of −0.23 (1/d, base e) on the average. The value corresponds to approximately 60% reduction in algal density in 4 d. The mathematical expression for suppression efficiency is,

$$e_H = (1 - e^{-0.23*\theta_H}) \qquad (1)$$

where e_H: suppression efficiency [–]: θ_H: hydraulic retention time in OPE [day].

The suppression rate constant was then used to derive a simple mathematical model for continuous system and solved at steady state. The hypotheses/assumptions made for the purpose of this study are:

(1) Each OPE is a completely mixed stirred-tank reactor.
(2) The system is at steady state.
(3) No algal growth in OPEs.
(4) Constant and equal influent and effluent flow rates.
(5) Algal density in the influent is constant.

Basic mass balance equation applied for each OPE is as expressed in Eq. (2).

$$V_i \cdot \frac{dX_i}{dt} = F_{in,i} \cdot X_{in,i} - F_{out,i} \cdot X_{out,i} - k \cdot X_i$$

or

$$\frac{dX_i}{dt} = \tau_i \cdot X_{in,i} - \tau_i \cdot X_i - k \cdot X_i \qquad (2)$$

where,

V_i : volume of the i-th OPE [m^3]
X_i : algal density in the i-th OPE [g/m^3]
$X_{in,1}$: algal density in the influent into i-th OPE [g/m^3]
$X_{out,i}$: algal density in the effluent from the i-th OPE [g/m^3] (=X_i by definition)
$F_{in,i}$: influent flow rate into the i-th OPE [m^3/d]
$F_{out,i}$: effluent flow rate from the i-th OPE [m^3/d] (=$F_{in,i}$ by definition)
$\theta_{H\,i}$: hydraulic retention time in the i-th OPE [day] $\left(= \frac{V_i}{F_{in,i}}\right)$
τ_i : reciprocal of $\theta_{H\,i}$ [1/d]
k : suppression rate constant [1/d] (a positive number)

However, because of the steady state assumption, constant flow rate, equal volume and equal influent algal concentration, Eq. (2) can be analytically solved to yield an algebraic equation with respect to X_i. The resultant equation for X_i is as shown in Eq. (3).

$$X_i = X_{in,i} \cdot \frac{\tau_i}{(\tau_i + k)} \tag{3}$$

Eq. (3) can further be generalized for a system of n OPEs with equal volume in series as in Eq. (4).

$$X_n = X_{in} \cdot \left\{ \frac{\tau_n}{(\tau_n + k)} \right\}^n \tag{4}$$

where,

n	:	number of identical OPEs in series in the process
X_n	:	algal density in the final effluent from the OPEs process
X_{in}	:	algal density in the influent to the OPEs process
θ_{Hn}	:	hydraulic retention time in each OPE [d] $\left(= \frac{V_i}{F_{in,i}}\right)$
τ_n	:	reciprocal of hydraulic retention time in each OPE ($= \frac{F_{in,i}}{V_i}$) [1/d]
k	:	suppression rate constant [1/d]

For the following considerations/evaluations, Eq. (4) was used both for single OPE process and multiple OPE in series process. It is assumed that the OPE process is implemented between the reservoir and a WTP as the pre-treatment process to reduce noxious cyanobacteria in the influent to WTP. It is also assumed in this calculation that the multiple OPEs are all identical and installed in series.

3.2. Comparison of single and multiple OPEs

A comparison was made with the constant total volume OPEs and a constant influent flow rate. As an expected outcome, suppression efficiency increases with increasing either suppression rate constant value (k) or HRT, or both (Fig. 2(a)). It is clearly seen that at higher k vales, suppression efficiencies form an exponential curve mainly at k value of 0.10 [1/d] and above; however, at very low k value of 0.10 [1/d] and below, a linear suppression ratio against HRT is achieved (Fig. 2(b)).

Table 1 shows the suppression ratio which represents ratio of algal density suppressed or inhibited upon treatment by single and multiple OPEs with various HRT and suppression constant values (k). Although suppression ratio seems to improve with

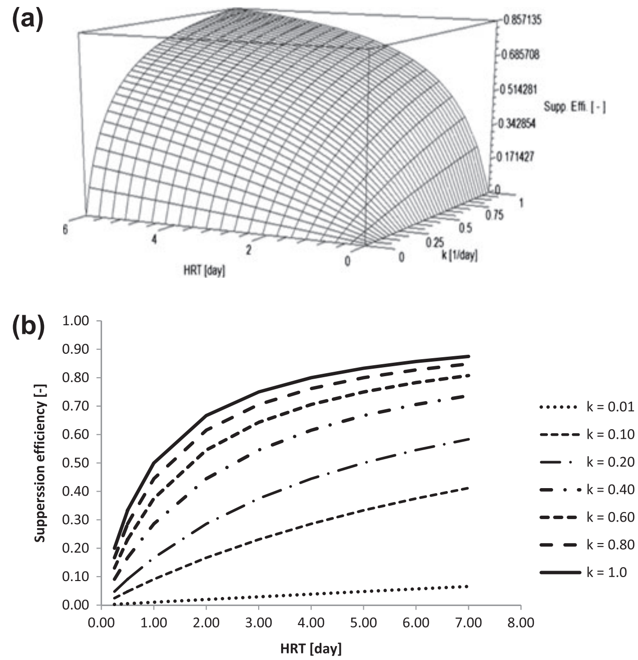

Fig. 2. Suppression efficiencies of single OPE (a) in 3-D graphical form in combination with various k values and HRTs (b) vs. HRTs with various k values.

increasing HRT for all single and multiple OPEs, OPEs in series processes appear to be much more efficient than a single OPE in terms of the total reactor volume. Thus, single OPE is less recommended from the view point of space utilization (Table 1 and Fig. 3).

The results also show that although multiple OPEs are better, the difference in efficiencies between 5 OPEs and 10 OPEs in series processes is not large disregarding k values (Fig. 3). Thus, using 10 OPEs may be less recommended as it does not improve much in terms of suppression efficiency. It appears that a system with 2–5 OPEs in series is more desirable than a single stage OPE and many OPEs in series systems.

Additional benefits of using multiple OPEs in series include that the number of OPEs operated can be adjusted depending on influent water quality, thus enabling a more flexible configuration, especially if water quality in reservoir varies seasonally and/or intake by WTP varies as the demand changes. When water quality is better, a lesser number of OPEs can be used, enabling the system to be more cost effective as it reduces operational and maintenance costs. It is also a standard engineering practice to include a redundancy in the system so that the OPE units can be operated alternately, thus enabling easy cleaning and maintenance. The additional reserve unit can be smaller in the multiple OPEs system than in a single-stage system. In this manner, performance efficiency

Table 1
Suppression ratio of single and multiple OPEs in series with various HRT and k values

		HRT [d]				
k [1/d]	No of OPEs (in series)	0.25	0.50	1.00	4.00	7.00
0.1	1	0.02	0.05	0.09	0.29	0.41
	2	0.05	0.09	0.17	0.49	0.65
	5	0.12	0.22	0.38	0.81	0.93
	10	0.22	0.39	0.61	0.97	1.00
0.2	1	0.05	0.09	0.17	0.44	0.58
	2	0.09	0.17	0.31	0.69	0.83
	5	0.22	0.38	0.60	0.95	0.99
	10	0.39	0.61	0.84	1.00	1.00
0.5	1	0.11	0.20	0.33	0.67	0.78
	2	0.21	0.36	0.56	0.89	0.95
	5	0.45	0.67	0.87	1.00	1.00
	10	0.69	0.89	0.98	1.00	1.00
1.0	1	0.20	0.33	0.50	0.80	0.88
	2	0.36	0.56	0.75	0.96	0.98
	5	0.67	0.87	0.97	1.00	1.00
	10	0.89	0.98	1.00	1.00	1.00

could be enhanced as well, making it a flexible and smarter system. On the other hand, smaller OPE units could be cheaper to build compared to larger ones. In addition, when water quality improves, the use of a single-stage OPE system or multiple OPEs without redundancy lead to existence of unnecessarily oversized OPEs making the system less cost effective and difficult to clean and maintain.

Further investigation is, however, necessary to evaluate whether or not a multiple system is more advantageous or disadvantageous in terms of capital cost, because the total capital cost depends on the efficiency and the dimensions of the sub-processes.

Figs. 2 and 3 are beneficial in describing relationship between suppression constant value or range with HRT and number of OPEs to obtain a desired suppression efficiency. Suppression efficiency is highest with $k = 1.0$ [1/d] and at HRT = 7 d (100% suppression) (Fig. 3(d)). At this suppression constant, $k = 1.0$ [1/d], a HRT of 1 d provides an acceptably high suppression efficiency ranging from 75 to 90% for 2–5 multiple OPEs. HRT of 3–5 d will be best, however this may not be practical for water treatment operations, especially when water supply demand is high. In addition, higher HRT accelerates the operational cost [6]. Suppression efficiency for 5 OPEs at $k = 1.0$ [1/d] seem to acceptably good for HRT 0.25, 0.50 and 1.0 d, respectively achieving 67, 87 and 97% (Fig. 3(d)). However, this is dependent on efficiency required and other related factors as discussed in the following sections.

When k is 0.5 [1/d] (Fig. 3(c)), HRT of 0.25 d or less is not at all recommended, especially if the water quality is poor and algal density is high. Instead, to be precise, for a suppression efficiency of 50%, HRT of at least 1.45 to 1.66 d will be required in combination with 2–5 OPEs. In the case where k is 0.2 [1/d] or less (Fig. 3(a) and 3(b)), at least HRT of 1 or higher will be required provided that algal density in the water is not too high.

3.3. HRT and suppression efficiency with k

Eq. (3) was used to estimate required HRT to achieve an adequate suppression efficiency such that $e_H = 0.5$. The relationship between total HRT and number of OPEs required for suppression efficiency of 0.5 is shown in Table 2. The k value of 0.23 [1/d] observed in the study was used in the estimation. k values of 0.50 and 1.00 [1/d] were also used for comparison.

It is obvious that, for a given k value, almost complete suppression is possible if HRT is designed long enough and/or a large number of OPEs are implemented; e.g. a system that consists of 10 OPEs in series can accomplish almost complete suppression in 10 d of HRT regardless of the suppression rate coefficient (Fig. 3). Such pre-treatment systems would be, however, economically infeasible and impractical.

As shown in Table 2, increase in number of OPEs used would result in reduction in total HRT. But the improvement from single OPE to 2–5 OPEs in series is more apparent than the increase in numbers of OPEs

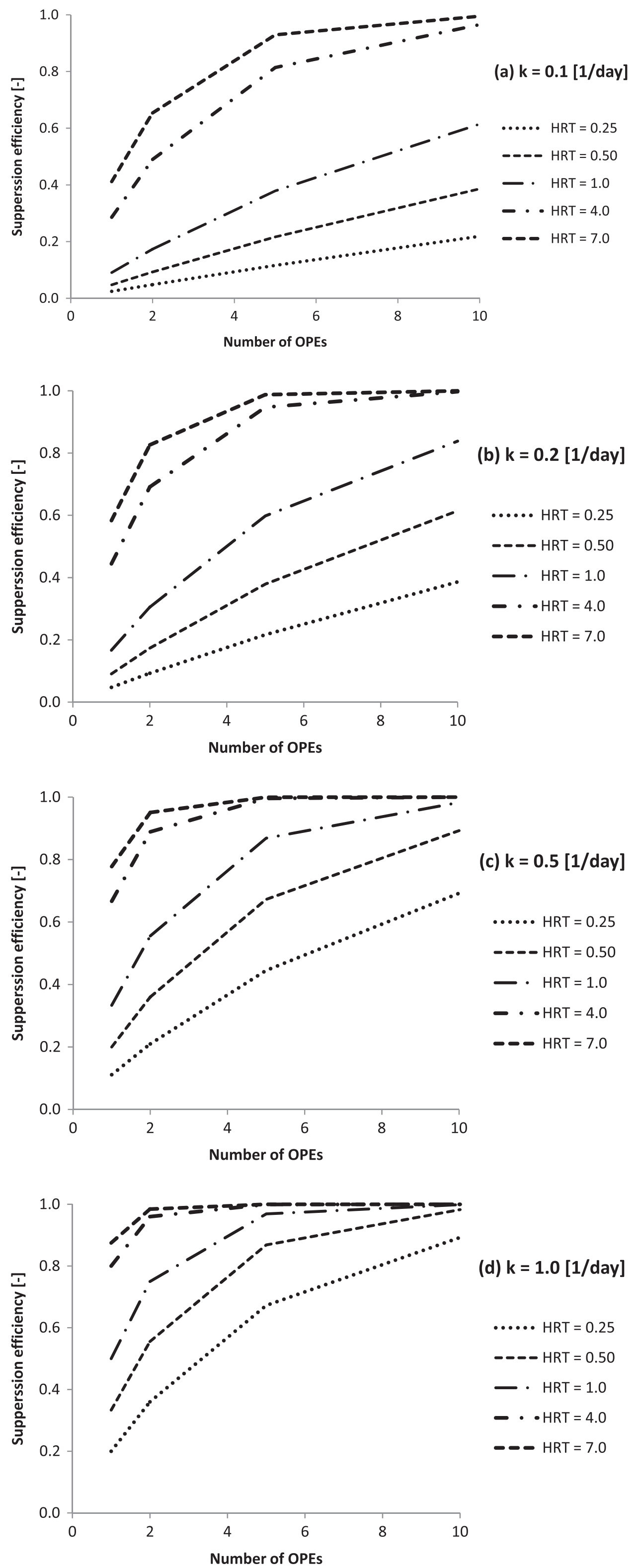

Fig. 3. Suppression ratio with number of OPEs and various HRT at (a) $k = 0.1$ [1/d] (b) $k = 0.2$ [1/d] (c) $k = 0.5$ [1/d] (d) $k = 1.0$ [1/d].

Table 2
Total HRT with numbers of OPEs required for $e_H = 0.5$

	Number of OPEs			
k [1/d]	1	2	5	10
0.23	4.35	3.60	3.20	3.10
0.50	2.00	1.66	1.45	1.40
1.00	1.00	0.82	0.75	0.70

from 5 to 10. These observations imply that if a set of physically separate OPE reactors are to be used, a set of 2–5 OPEs in series would be a sensible configuration. However, if a single long-channel like reactor design, which can be considered as a plug-flow reactor, is possible, it could be a practical reactor design to consider. Further investigation and engineering considerations are necessary.

3.4. Comparing HRT and suppression efficiency with k from different OPE experiments

Various OPE electrolysis systems were compared based on algal removal trends and percentages. Suppression constant, k [1/d], was calculated for each of these and compared with result from our study. However, operational conditions of these OPE systems differ slightly and could lead to the differences in these values. An average of 0.59 with a range of 0.19–0.99 [1/d] k values were obtained from results of six algal species by OPE electrolysis, including this study (Table 3).

Dictyosphaerium subspicatus from Cui [11] and *Aphanizomenon flos-aquae* from this study had the lowest k value, indicating its difficulty in removal compared to other species. The suppression efficiency of these two species and their choice of number of OPEs and HRT will be somewhat as shown in Fig. 3(b) and Table 2. For example, when k value is 0.23 [1/d], to obtain a 50% suppression efficiency in combination with 2–5 number of OPEs, a HRT of 3.20–3.60 d will be required (Table 2). However, for reduction of HRT for a more cost-effective and practical treatment, enhancement of operational efficiency is done by changing operational factors. Some relevant factors as current density and electrode materials with regard to change in electrolysis performance are described in Sections 3.5 and beyond.

For suppression of *Microcystis aeruginosa*, which has k value of 0.76 [1/d], a combination of 2–5 OPEs with approximately 1.00 to 1.35 d HRT will be required to obtain 50% suppression efficiency.

Table 3
Suppression constants of various algal removal systems

System	Species	Suppression constant, *k* [1/d]	References
OPE electrolysis (Nafion membrane)	*Aphanizomenon flos-aquae*	0.23	This study, 2014
	Microcystis aeruginosa	0.76	Gao et al. [7]
	Phormidium tenue	0.95	Cui [11]
	Aphanizomenon smithii	0.99	
	Dictyosphaerium subspicatus	0.19	
	Phormidium tenue	0.40	Imazato [10]
Ozonation (corona discharge ozone generator)	*Microcystis aeruginosa*	39.9	Miao and Tao [18]
Ti/RuO_2 electrode system with NaCl liquid electrolysis	*Microcystis aeruginosa*	0.18	Xu et al. [13]

However, for *Phormidium tenue* and *Aphanizomenon smithii* [11], higher suppression efficiency will be obtained with lesser HRT compared to other species tested. Only 0.75 d HRT required with 5 OPEs to produce a suppression efficiency of 50%.

In general, the operational conditions were different for each study, and this may have influenced the difference in the *k* values obtained. For example, for *A. flos-aquae* and *A. smithii*, there was a large difference between the suppression constant obtained. This may be influenced by variation in the algal density determination method. In our study, counting was done based on number of filaments/ml; however, in Cui [11], counting was done based on cells and not filaments. Filaments could be long or short and may contain few or many cells. Since number of cells in each filament varies, the number of filaments and cells are not proportional to each other.

This study suggests to utilize suppression constant as a range and not an individual value. For example, 0.23–0.99 [1/d] for *Aphanizomenon* sp. as some minor variation even from similar operational conditions would be expected, this is to account for measurement uncertainties for scale-up of the OPE system.

These were compared with results from two other types of algal removal system, and they are ozonation using corona discharge ozone generator and Ti/RuO_2 electrode system with liquid NaCl electrolytes, which removed cyanobacteria at a *k* value of 39.9 and 0.18 [1/d], respectively.

Ti/RuO_2 electrode system requires use of salt electrolytes which produces impurities and high algal sludge [3,8]. In addition, Ti/RuO_2 used for disinfection of *Legionnaire* bacteria up to 99.5% showed the need for extremely high voltage of up to 1 kV for a treatment volume of only 500 ml [17]. On the other hand, direct ozonation using corona discharge generator, at a dose of 5 mg/L of ozone, removed 91.2% of *M. aeruginosa* upon 60 min of reaction time [16].

Ozonation is the most powerful oxidants among the conventional oxidation processes and able to remove cyanobacteria very efficiently [18,19]. However, electrolysis produces six times more ozone than corona discharge process [22]. In addition, electrolysis, an advanced oxidation processes (AOPs), produces a combination of peroxides and ozone, known as peroxone, which have a much higher oxidation efficiency. Therefore, OPE electrolysis, as a result from the peroxones, is more advantageous in damaging organic molecules causing lyses of potentially harmful cyanobacteria such as *Aphanizomenon* sp. and *Microcysis* sp. [7,8,20,21], as well as degrading its metabolites (MCs, DOC and VOC, for example, odour-causing 2-MIB and geosmin) [16,21]. This disregards the need to remove cyanobacteria cells or filaments prior to degradation of metabolites [18]. Additionally, other AOPs, such as those using iron or hydrogen peroxide (Fenton) will raise operational cost, and may create other effects in the systems being chemicals [19]. OPE electrolysis is thus an all-in-one pollutant removal technology and strongly recommended as a more flexible, self-sustainable and environmental-friendly system. However, some relevance factors with regard to electrolysis performance efficiency are to be considered. These are described in Sections 3.5 and beyond.

3.5. Size of OPE and volume of water with K_La and suppression efficiency

Apart from suppression constant (*k*), number of OPEs with HRT as crucial determinants for up-scaling

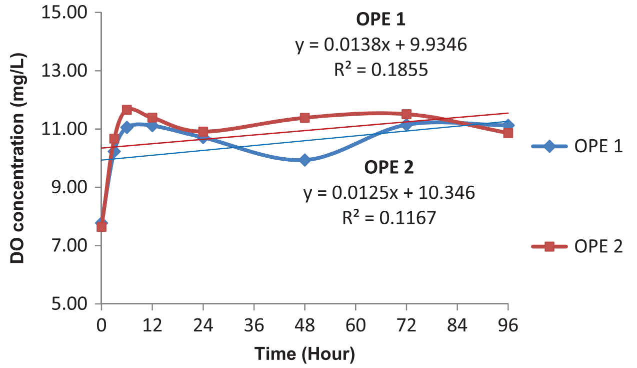

Fig. 4. Net oxygen production rate for OPE systems (in duplicate) at 25°C.

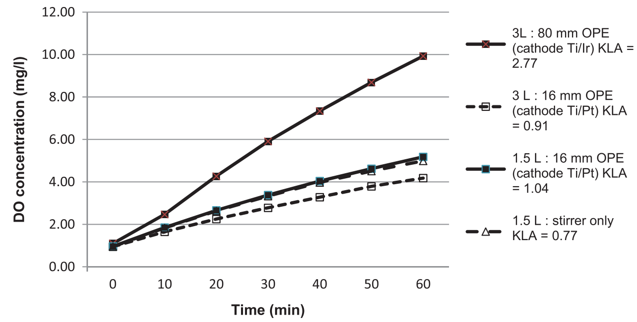

Fig. 5. DO concentration and K_La produced by OPEs of different size (16 mm and 80 mm) with different volumes (1.5 and 3 L) of MilliQ water.

of a system, size of OPE and volume of water to be treated is studied in terms of its influence towards cyanobacteria suppression efficiency.

Based on the batch experiment, oxygen production rate in 8,000 filaments/ml cyanobacteria-spiked medium is calculated as 0.0138 mg/L/hour and 0.0125 mg/L/hour for OPE 1 and OPE 2, respectively (Fig. 4). This value is the net oxygen achieved after 4 d of treatment despite consumption (during respiration) and production (during photosynthesis) by the cyanobacteria, and is 76 times lesser than oxygen achieved in the absence of cyanobacteria ($K_La = 1.04$ mg/L/hour). Though the K_La and net oxygen production rate achieved shows that electrolysis is useful in maintaining good quality water with sufficient oxygen levels, this is not the mechanism responsible to remediate the cyanobacteria filaments as explained in another paper [13].

Apart from oxygen, OPE produces reactive oxygen species (ROS) such as O_3 (ozone), $O_2 \cdot^-$ (superoxide anion radical), OH· (hydroxyl radical), $HO_2 \cdot$ (perhydroxyl radical), H_2O_2 (hydrogen peroxide) and $^1O_2$ (singlet oxygen) in a series of reactions [12]. It is the ozone produced from a direct reaction and hydroxyl from an indirect reaction which is responsible as the mechanism of suppression [7–8,16]. A dosage of 1–5 mg/L ozone resulted in cell wall alterations [4], and the damage was higher with the increase of the ozone dosage [18]. Algal cells were found to be injured and could not survive at level 3 mg/L and beyond [16].

The exact relationship between gas production (oxygen and its radicals) or K_La with oxygen radical (mainly ozone and hydroxyl) production is not known. However since OH and ozone as well as K_La which are both proportional to suppression efficiency as shown separately in previous studies [7,8,12], K_La, is thus used to express suppression efficiency.

Based on K_La experiments conducted prior to the suppression experiment in this and previous study [10], K_La values produced by OPE of the same size (16 mm) did not significantly change when volume of MilliQ water was increased from 1.5 L to 3 L (Fig. 5). Although a different anode material is used in the 80 mm OPE and 16 mm OPE, the K_La values for Ir and Ti tested using OPE unit of same size (16 mm) did not differ significantly [12], thus enabling comparison to be made.

K_La value was found to increase more than twice or almost three times when a larger unit of OPE (80 mm) was used. As larger unit would have larger surface area, more gas with larger amounts of ozone and hydroxyl radicals produced, leading to greater suppression efficiency. This implies that cyanobacteria suppression efficiency improves with larger OPE size. It should be noted that as the cost of a larger OPE unit is higher, it may be more cost effective to adjust other operational factors, such as current density, flow rate and HRT, to improve suppression efficiency rather than increasing the size.

3.6. *Stirring effects and organics influencing suppression efficiency*

An additional comparison was made for coefficient value between stirring without OPE (0.77 mg/L/hour) and OPE with stirring (1.04 mg/L/hour). This comparison showed that dissolution of oxygen from air–water interface into the water is substantially enhanced by effects of stirrer alone. However, algal suppression did not occur in control, instead there was a positive growth. Thus, oxygen source or mixing of water alone, as a result from mechanical aeration, is ineffective in algal suppression.

In the case of OPE treatment, mild stirring is necessary to ensure the algae are sufficiently mixed in the treatment tank and subjected to equal exposure or contact with oxygen-reactive species produced by OPE for effective suppression [7,8]. Alfafara et al. [1] provided an insight as to how effects of mixing or stirring should be adjusted or reduced when higher electrical input or current density is applied. Higher electrical and current input naturally introduces some turbulence and enhances gas evolution, thus care to be taken to not allow too much dispersion to water–air interface leading to reduction in the performance [1]. In real practice, such considerations are to be incorporated.

In addition, for effective operation, there may be an optimal depth at which the system should be placed from the surface of the water, not too near the surface to limit any gas and radicals from dissipating into the water–air interface but dissolved into the water [7,8]. It is recommended to install the OPE at the bottom enabling oxygen radicals to flow upwards as nano-bubbles. Study on electrolytic flocculation and electrolytic flotation proved usage of electrodes most efficient when at the bottom as it enabled contact of algal clumps with the hydrogen bubbles released for best flocculation results [1].

Considering the difficulty of measuring radicals [7,8,12] as compared to the ease of measuring dissolved oxygen, it is suggested to obtain the relationship between the production of these radicals, mainly ozone and hydroxyl with OPE gas production rate or K_La as an indirect measurement for scale-up or monitoring purpose.

Further investigation is required in the future to determine exact relationship between volume of cyanobacteria-spiked water to be treated and size of OPE with K_La and/or radical production as well as suppression efficiency. However, net oxygen production rate values compared to K_La, apart from relationship with current density, OPE dimension, volume of water and electrode materials will also be dependent on additional factors mainly behaviour and density or loading of cyanobacteria in the medium to be treated. Thus, relationship between suppression efficiency with K_La, gas production rate (prior to treatment), net oxygen production rate (upon treatment), OH and ozone production based on various cyanobacteria type and loading levels needs investigation for scale-up purpose. In addition, scale-up has to consider the natural water quality from the lake or reservoir with the mixed algae, which is extracted into the treatment tank where OPE unit(s) are installed.

Some crucial water quality factors of concern or those interfering or influencing cyanobacterial suppression also require consideration. Interferences from ozone production by-products, such as dissolved organic carbon (DOC) and volatile organic carbon (VOC), may lower algal metabolites suppression efficiency [18]. Study showed that 1 mg/L ozone level lead to increase in DOC of algae suspension from 0.34 to 1.03 mg/L, while 3 mg/L and 5 mg/L ozone caused an increase in DOC to 1.98 mg/L and 2.56 mg/L. DOC retards degradation of microcystins (MCs) as it competes with MCs by reacting with ozone. In addition, higher level of ozone 5 mg/L produces a considerable amount of VOC maybe from algal metabolites or ozonation by-product [18]. Whether or not DOC and VOC and other water pollutants lower the efficiency of OPE in suppressing the algae itself, further investigation is needed. Another study showed total organic matter (TOC) causing reduction of algae removal in electrolysis performance [1]. Thus, further work on interference of organic matter with regard to effects to suppression efficiency is suggested to eventually incorporate a correction value to the mathematical simulation scale-up formula.

Electrolysis was also shown to remove nutrients and organics such as T-N, T-P, NH_4-N and COD in domestic wastewater and pond water, while removing 100% of chlorophyll-a [3]. This provides added advantage to OPE as its ability in removing nutrients and biochemicals as this may reduce the need for high dosing in coagulation as well as treatment cost of subsequent water treatment process. This enables higher water treatment efficiency provided that the electrolysis system is well implemented and maintained. However, currently, not much maintenance is required except for cleaning of using MilliQ or distilled water and change of membrane only if suppression efficiency reduced. Monitoring indicators should be established, such as K_La value or other better indicators, to ensure efficiency is maintained throughout electrolysis.

3.7. Electrode materials and current density

Previous studies on this OPE system tested the relationship of K_La with current densities and electrode materials [7,8,12,13]. Electrode materials, such as Ti/Ir and Ti/Pt, have been successfully tested and proven suitable as anode and stainless steel for cathode based on conductivity, sustainability, cost effectiveness and easy availability of the electrode materials [7,8,12,22]. Electrode materials have also proven to influence ozone production [22]. Curteanu et al. [5] demonstrated that aluminium electrodes were much more effective than stainless steel for an integration of electro-coagulation and electro-flotation process to treat algae in wastewaters. This study showed stainless steel only functioned for electro-flotation part of the process, thus making it ineffective. Furthermore, as the mechanism of the electrolysis is different, finding of Curteanu et al. [5] is not applicable to OPE electrolysis.

In our study, stainless steel was used only for cathode similar to electrolysis used in another wastewater study [6]. Hamatani [12] proved that for OPE electrolysis, stainless steel was found to be significantly better in producing K_La compared to aluminium, thus making it suitable for this electro-oxidative system. Meanwhile, K_La for Ir and Pt was higher than stainless steel [15]. This could be the reason for the lower suppression constant k value of 0.23 [1/d] obtained in this study compared to previous studies (Table 3). This study used stainless steel for cathode, instead of Ti/Pt for both anode and cathode [7,8,22] to further reduce the cost of the OPE, especially for developing or low-income countries. However, use of stainless steel for cathode should not cause a substantial difference and rather acceptable for the intended use.

Previous studies demonstrated that when higher current density is used, suppressive effect [1] is enhanced along with overall rise of oxygen production as well as OH radical formation rate [7,8,13]. Meanwhile, at constant current density, cyanobacteria suppression is increased with electrolysis time [7,8]. Gao et al. [8] demonstrated that rate constant of OH radical production with current density was 0.174 nMs^{-1} whereby at 40 mA/cm^2 OH production rate of 0.1 nMs^{-1} is achieved. However, this study could not detect ozone level as it was under the detection limit of the method used. Alfafara et al. [1] discovered that higher power source and current intensity removed chlorophyll-a loading at a higher rate; however, this finding could not be directly applied as it was for an integration of electro-flocculation and electro-flotation, which are different in terms of principle and mechanism to remove algal cells. In addition, another study on wastewater highlighted that the efficiency of current density was limited by other factors and effects of electrolysis such as rise in temperature, although this could also be regarded as a benefit in enhancing suppression reactions [5]. However, in our study, there was no obvious change in temperature. Nevertheless, a relationship between current density and suppression efficiency has to be established to enable a more precise scale-up.

On the other hand, Han et al. [22] showed that ozone production current efficiency increased with current density, maximizing to 13–14% at 1,500–2000 mA/cm^2. Meanwhile, at current density of 200 mA/cm^2, 3% of O_3 production efficiency was produced with 3.3 V and 25˚C operation using β-PbO_2 anode and Pt cathode [22]. If this relationship is applied in our study, at a current density of 40 mA/cm^2, percentage of ozone production current efficiency would approximately be 0.6%. This low-current density of 40 mA/cm^2 was nevertheless able to produce sufficient ozone and hydroxyl levels to suppress 60% of *Aphanizomenon* sp. in 4 d by decomposing organic molecules and removing coloration [18]. In addition, the low ozone levels produced by OPE into the water–air interface were unable to cause health hazard to operators [12].

However, based on existing rate of suppression, there may be a need to enhance removal rates without incurring too much rise in operation. Moderate current density between 40 and 100 mA/cm^2 is recommended to ascertain relationship between current density and suppression constant and efficiency, as previous studies did not address this relationship [7,8]. Some studies showed the need for very high current densities to produce sufficient ozone [22], leading to higher energy consumption. Current density in our study is much lower than other studies, enabling low energy consumption.

3.8. Voltage

Voltage is a parameter of concern as it was found to increase in many situations including with reduction in water temperature, increase in flow rate of water and in the presence of seawater intrusion [14,22]. The membrane is poisoned, especially anodic side, by Na^+ ions from seawater causing a decrease in specific conductivity, which leads to rise in cell voltage at constant current density [13–15]. In addition, it can cause reduction in current density leading to degradation of electrolysis cell performance [13].

The advantage of OPE electrolysis from this and other studies [7,8,22] is the voltage remained constant after achieving a plateau at constant current density.

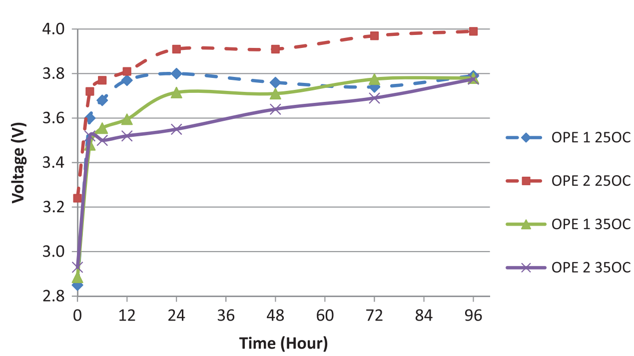

Fig. 6. OPE voltage at 25 and 35˚C for 2 duplicate OPE units, OPE 1 and OPE 2 ($n = 2$).

Initial voltage of both OPE units was 2.8–3.3 V and gradually formed a stable plateau from the 24th hour onward to a maximum voltage of within 4.0 V for both water temperatures 25˚C and the warmer 35˚C (Fig. 6). Similarly, maximum voltage of 4.0 V was attained in the suppression of *M. aeruginosa* species at a k value of 0.76 [1/d] [7,8]. Additionally, in another study where current density of 2,500 mA/cm^2 produced an ozone production current efficiency of 13.5%, maximum 4.0 V was achieved as well [22]. The ability of OPE system to operate with low voltage even for different species is an added advantage provided that it is not exposed to salt [14,15].

4. Conclusion

This study provided great insights on combination between k, number of OPEs and HRT required to achieve the best or required suppression efficiency of algae or cyanobacteria. HRT, which is also dependent on water treatment cycle time or treatment demand, should be preferably short, otherwise operational factors have to be improved in order to obtain better suppression constant such as closer to 1.0 d^{-1} or even higher if necessary. In terms of number of OPEs, multiple OPEs in series were found to more desirable, effectively 2–5 OPEs. In order for cost effectiveness, smaller size OPEs and smaller volumes of multiple OPEs are desirable. Additionally, for up-scaling purpose, size or dimension of OPE could be determined based on the cost of making it. In addition, water supply demand information along with WTP maximum or projected treatment capacity information will enable the determination of total volume to be treated with the total water cycle rate, which are both related to flow rate of water to be treated in the WTP.

A combination of oxygen transfer coefficient rate or radical production rate, initial cyanobacteria density or loading, hydraulic retention time, flow rate, volume of water to be treated, current density and electrolysis time are necessary for scaling up for a system using OPE of fixed or variable dimension and with predetermined electrode material. It is necessary to balance all of these factors with production level of ozone and radicals, which is within health safety limit.

In the case where a variety of algae are polluting the water, then decision should be based on the range of suppression constants to ensure suitable suppression efficiency to all persistent and non-persistent types. Identification of suppression constants of mixed cultures of filamentous and unicellular is suggested. It may be necessary to identify the worst-case scenario of the algal blooms in terms of density and type of algae. Knowledge on seasonal variation such as during low water level (such as during dry season) and higher water level (such as during wet season) could be useful. A regular monitoring programme to monitor density and type or genera is strongly recommended for best treatment.

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