Study on the inactivation of cyanobacteria bloom and the change of phosphorus and nitrogen through electrolysis

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Abstract

This study was conducted through elelctrolysis since titanium (Ti) as cathode and RuO_2-IrO_2 coating stabilized (RuO_2-IrO_2/Ti) as anode to control the cyanobacteria bloom and the remediation of water exposed to cyanobacteria bloom events. The order of influence on theoretical energy consumption of algaecide was electrode spacing > electrode voltage > electrolysis time through the orthogonal test method, considering the energy consumption of algaecide, the electrode spacing of 60 mm, electrode voltage was 30 V and electrolysis time was 12 hours were the most appropriate factors to removal cyanobacteria bloom. The strong acidic environment produced by anode enhanced the concentration of production of ·OH and other strong oxidizing substances which were the main reasons to remove cyanobacteria bloom; phosphorus and nitrogen factors causing algal blooms were also analyzed, the electrolysis reaction was conducive to the transformation of organophosphorus in cyanobacteria to DIP in water and some DIP was deposited on the cathode through electro-deposited enhanced the removal of P in water with the prolongation of electrolysis time, and meanwhile it was beneficial to reduce the total nitrogen (TN) and ammonia nitrogen (NH_3-N) in the water. Thus, elelctrolysis was an effect way to remove cyanobacteria bloom and recovery P as the concentration was higher.

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Abstract

This study was conducted through elelctrolysis since titanium (Ti) as cathode and RuO_2-IrO_2 coating stabilized (RuO_2-IrO_2/Ti) as anode to control the cyanobacteria bloom and the remediation of water exposed to cyanobacteria bloom events. The order of influence on theoretical energy consumption of algaecide was electrode spacing > electrode voltage > electrolysis time through the orthogonal test method, considering the energy consumption of algaecide, the electrode spacing of 60 mm, electrode voltage was 30 V and electrolysis time was 12 hours were the most appropriate factors to removal cyanobacteria bloom. The strong acidic environment produced by anode enhanced the concentration of production of $\cdot OH$ and other strong oxidizing substances which were the main reasons to remove cyanobacteria bloom; phosphorus and nitrogen factors causing algal blooms were also analyzed, the electrolysis reaction was conducive to the transformation of organophosphorus in cyanobacteria to DIP in water and some DIP was deposited on the cathode through electro-deposited enhanced the removal of P in water with the prolongation of electrolysis time, and meanwhile it was beneficial to reduce the total nitrogen (TN) and ammonia nitrogen (NH_3-N) in the water. Thus, electrolysis was an effect way to remove cyanobacteria bloom and recovery P as the concentration was higher.

Keywords: Cyanobacteria bloom; Electrolysis; P removal; Electro-deposition; N transformation

1 Introduction

Cyanobacteria bloom is a serious threat to the ecological structure and ecological function of lake ecosystem (Michalak et al., 2013; Müller et al., 2017; Huisman et al., 2018; Cusick et l., 2020; Rousso et al., 2020). China's Taihu Lake, Dianchi Lake and Chaohu Lake also have frequent outbreaks of "water bloom" (Shi et al., 2015; Zhang et al., 2019). Large number of cyanobacteria will increase the turbidity of lake water, thus reducing the water light level and inhibiting the growth of underwater vegetation and population quantity and pose a threat to drinking water, irrigation water, fisheries and recreation (Liu et al., 2013; Liu et al., 2019;

Burdic et al., 2020). Recently, a variety of techniques such as UV irradiation, ultrasonication, aeration and circulation, filtration, coagulation, sedimentation and hydrogen peroxide, algaecide and algicidal peptides, and algicidal bacteria has been developed to minimize the harmful effects of cyanobacterial blooms that are based on the removal anddestruction of the cyanobacterial community (Meglič et al., 2017; Kim et al., 2020). Although these are only efficient for the removal of cyanobacteria, but it is difficult to remove the secondary substances such as phosphorus (P) and nitrogen (N) nutrients, cyanobacterial toxins, peculiar smell substances after the decay of cyanobacterial cells.

Electrochemical oxidation was attracting much attention as an cyanobacteria removal technologies where variety of high catalytic activity of reactive oxygen species (ROS), active chlorine and sulfate radical and other strong oxidation substances can be generated in-situ and at controllable rates and harmful by-products formation was largely avoided, and more and more attention has been paid to the removal of cyanobacteria by electrolysis due to its simplicity and efficiency in cyanobacterial cell inactivation, degradation of toxins , taste and odor compounds. Recently, Ti/IrO_2, Pt/Ti and boron-doped diamond (BDD) electrode were used to remove cyanobacteria and cyanobacterial toxins (Meglič et al., 2017; Sanz Lobón et al., 2017; An et al., 2019; Belal et al., 2019). Moreover, most researches focused on the removal of cyanobacterial and secondary substances and to the best of our knowledge there were few studies about the removal of high concentration of cyanobacterial bloom and the P and N nutrients removed during the inactivation of cyanobacteria by electrolysis since ROS and other oxidants produced by electrochemical oxidation also lead to the release of P mineralization and N transformation and (Jeon et al., 2014). As the oxidation and reduction role of anode and cathode caused by electrolysis also conducive to the transformation and removal of nitrogen (Yao et al., 2019). As for P, the main components of electrodeposited P are calcium phosphate rock ($CaHPO_4 \cdot 2H_2O$, DCPD) and anhydrous dicalcium phosphate ($CaHPO_4$, DCPA) could accured on the cathode (Blanda et al., 2016; Metoki et al., 2016; Vladescu et al., 2017). But there were no more details about the removal of P and N during the electrolysis inactivation of cyanobacteria bloom.

The objectives of this research were to verify the effectiveness of electrolysis inactivation in high concentration of cyanobacteria bloom; to show the priority influence of processing factors such as voltage, electrolysis time, distance of electrode and energy consumption; the P in vitro and in cyanobacteria, and the electrodeposition material of P was also dectecd to explore the transformation of organic and inorganic P, and the concentration of different forms of N during the electrolysis process were also determinated during the inactivation of cyanobacteria bloom to analyze the transformation and removal path of P and N nutrients; simultaneously the variation of ORP, pH, DO and salt of anode and cathode zone during the electrolysis treatment wrere detected to analyze the change of microenvironment effected the inactivation of cyanobacteria bloom. The results indicate potential use for the application of electrolysis methods for the control of cyanobacteria bloom and has the additional advantage that

it provides simultaneous destruction of the cyanobacteria and removel of the nutrients of P and N which caused cyanobacteria bloom.

2 Material and method

2.1 Experimental device set up

The device for electrolysis inactivation of cyanobacteria bloom and removing P and N by electrolysis was manufactured with plexiglass as seen in Fig. 1 with a total volume of 6.25 L and the size was 25 cm long, 15 cm wide and 15 cm high, totoal of 3.75 L cyanobacteria bloom collected from the West Bank of Taihu Lake (119°56' E, 31°19' N) during the outbreak period of cyanobacterial bloom. The physical and chemical indexes of water body are shown in Table 1. The density of cyanobacteria was about 3 $\times 10^8$/mL. The cathodes used in the experiment were all pure titanium (Ti) electrodes, and the anodes were Ti based RuO_2-IrO_2 coating stabilized electrode (RuO_2-IrO_2/Ti) mesh electrodes, both are 250 mm long×150 mm wide×2 mm thick and the effective working area of the electrode was 37.5 cm^2. Anodes and cathodes were all purchased from Suzhou Yunrui Environmental Technology Co., Ltd. Both anodes and cathhodes were vertically inserted into the devices as the electrode distance could be adjusted to 30 mm, 60 mm, 90 mm and 120 mm to analyze its impact on the inactivation of cyanobacteria bloom. The electrodes were connected using a crocodile clip to a Model KXN-3020D DC regu-lated power supply (Zhaoxin Electronic Instruments and Equipment Co., Ltd., Shenzhen, China) with a voltage ranging between 0 V and 30 V and an amperage between 0 A and 2 A and provided a voltage of 15 V, 20 V, 25 V and 30 V for electrolysis. After each test, the electrodes were immersed in acid solution (1.0M HNO_3) for one day. After pickling, take it out and put it into ultrasonic cleaning machine (KH3200DB, Kunshan Hechuang Ultrasonic Instrument Co., Ltd) as the frequency was 50 kHz for half an hour, and finally wash the electrodes with deionized water. The experimental apparatuses were maintained within a temperature range of 25 ℃ to 30 ℃.

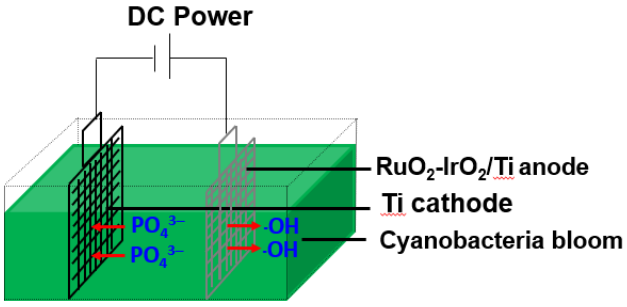

Figure 1 Schematic diagram of the electrolysis removal device of cyanobacteria bloom

Table 1 The basic properties of cyanobacteria bloom water in Taihu Lake

Water quality parameters	Concentration	Water quality parameters	Concentration
NH_3-N (mg/L)	18.5	Salt (ppt)	0.23
NO_3^--N (mg/L)	2.97	DO (mg/L)	1.47
NO_2^--N (mg/L)	0.32	ORP (mV)	169.3
TN (mg/L)	43.95	pH	6.65
TP (mg/L)	7.08	Ca^{2+} (mg/L)	27.35
PO_4^{3-}-P (mg/L)	1.05	Mg^{2+} (mg/L)	5.21

2.2 Water sampling, morphology and composition analysis of precipitates

2.2.1 Water sampling and analysis

Water samples of cyanobacteria bloom were collected from the reactor every one hours to determine the physical and chemical indicators of water quality. The pH and DO were immediately measured by a portable Hach HQ30d multi-parameter analyzer, a PHC101-30 pH electrode, and a LDO101-03 DO electrode (all from Hach Company, Loveland, CO, USA), ORP values and salinity were immediately measured using a multi-parameter water quality YSI Pro-Plus (YSI Inc., Yellow Springs, OH, USA). chlorophyll-*a* (Chl-*a*) concentrations (Acetone extraction spectrophotometry), NO_3 -N (dihydrochloride), NO_2 -N (N-(1-naphthyl) ethylenediamine dihydrochloride), NH_3-N (natrium reagent), TN (alkaline potassium persulfate digestion), TP (Digestion-Mo-Sb antispectrophotometric method) and PO_4^3 -P (ascorbic acid method) were measured using an ultraviolet and visible (UV-Vis) V1800 spectrophotometer (Shimadzu Corp., Kyoto, Japan) after the corresponding standard pretreatment and reagent addition were completed. All the testing procedures were according to Standard Methods for the Examination of Water and Wastewater by the Ministry of Ecology and Environment of the People's Republic of China (The State Environmental Protection Administration, 2002).

2.2.2 Morphology and composition analysis of precipitates

At the end of the experiment, the precipitates deposited on the Ti mesh cathodes were collected. The scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) were used to observe the surface morphology and composition of the precipitates.

2.3 Data treatment and statistical analysis

All data analyses were performed in triplicate, and the data were expressed as mean ± standard errors. To evaluate the inactivation of cyanobacteria bloom

by electrolysis, current density (mA) and energy consumption ($W \cdot h$) were all analyzed, according to the following formulas.

$$I = (\sum Ii \times t)/t \quad (1)$$

$$W = U \times I \times t \quad (2)$$

where I (mA) represents the mean current value through the anode and cathode during the electrolysis time; *Ii* (mA) represents the instantaneous current value; *t* represents the time intervals of current recording; t (h) represents the electrolysis time; W ($W \cdot h$) represents the power used by electrolysis; U (V) represents the voltage of electrolysis respectively.

The concentrations (mg/L) of Chl-*a*, NO_3 -N, NO_2 -N, NH_3-N, TN, TP, PO_4^{3}-P and energy consumption ($W \cdot h$) by electrolysis were performed with SPSS 23.0 (SPSS Inc., Chicago, IL, USA), the significant differences of energy consumption ($W \cdot h$) between treatments were determined by an analysis of variance (ANOVA) followed by post-hoc testing using Tukey's HSD test. A *p* value of less than 0.05 was used to determine if the differences were statistically significant use one-way ANOVA by Microsoft excel 2016.

3 Results and discussion

3.1 Analysis of electrolysis factors on inactivation of cyanobacteria bloom

Oxidation of organics and oxygen evolution take place on anode electrode mediated by hydroxyl radicals (such as radical $\cdot OH$) that are generated from the discharge of water during the electrolysis process. The radical $\cdot OH$ is a powerful non-selective oxidizing agent that can react with cyanobacterial cells, with the production of dehydrogenated or hydroxylated by-products that can then undergo total mineralization. Moreover, radical $\cdot OH$ is responsible for the generation of ROS, such as O_3 and H_2O_2, which can also then react with cyanobacterial cells and provoke irreversible cell damage to cyanobacteria cell (Li et al., 2015; Gao et al., 2018). Under the condition of given electrode size and material, the concentration of strong oxide generated was directly proportional to the current intensity as electrochemical oxidation can destroy cyanobacterial cell structure by producing strong oxides. Researchers found that the cell density and optical density of *Microcystis aeruginosa* decreased proportionally to the current density and the detention time (Liang et al., 2005). In this experiment, voltage, electrode spacing and electrolysis time were the main factors influencing the current size and energy consumption by electrolysis. The orthogonal test method was used to study the influence of voltage, electrode spacing and electrolysis time on the inactivation efficiency of cyanobacteria bloom and obtain the best operation parameters.

It could be seen from the table S1, S2, S3 and S4 that the range R values corresponding to electrode voltage, electrode spacing and electrolysis time were 2.17,

3.46 and 1.90, respectively. Therefore, the order of influence of each factor on theoretical energy consumption in activation of cyanobacteria bloom was electrode spacing > electrode voltage > electrolysis time. Then, the single factor of electrode spacing and electrode voltage were carried out respectively, and the optimal working conditions of the experiment were determined by combining with the above orthogonal experiments. With the decrease of electrode spacing, the electric resistance between electrodes decreased, the electric current increased which might coused the yield of strong oxide substances increased, which greatly shorten the time of the inactivation of cyanobacteria bloom.

At different electrode spacings from 120 mm, 90 mm, 60 mm and 30 mm, the corresponding average power was 1.38 W, 1.83 W, 2.79 W and 4.79 W, respectively. After 12 hours of elelctrolysis, the Chl-*a* removal rate was 25.7%, 36.1%, 61.7% and 81.4%, respectively (Fig. 2a). Thus, under the premise of constant electrode voltage, the electric resistance between electrodes decreased with the decrease of electrode spacing which caused a rise in electric current. Higher electric current lead to the increase of reactive oxygen species production, which greatly shortened the electrolysis time and more cyanobacteria bloom were likely to be inactivated.

As the electric energy consumed for each electrode spacings from 120 mm, 90 mm, 60 mm and 30 mm reduction of 1% Chl-*a* were 0.643 $W \cdot h$, 0.607 $W \cdot h$, 0.543 $W \cdot h$ and 0.706 $W \cdot h$, respectively (Fig. 2b). It could be concluded that the energy consumed in the inactivation process of cyanobacteria bloom by electrolysis was inversely proportional to the electric resistance due to the heat production under the condition of constant electrode voltage. At the same time, too small electrode spacing made the electric resistance in the electrical path smaller. Therefore, too small electrode spacing would cause the waste of electric energy in the thermal reaction. Considering the energy consumption, the electrode spacing of 60 mm was the most appropriate electrode spacing.

Figure 2. Change of Chl-*a* in water (a) and energy consumption (b) under different electrode spacing of 120 mm, 90 mm, 60 mm and 30 mm

To study the effect of different voltage on the inactivation of cyanobacteria bloom, the voltage was setted to 15 V, 20 V, 25 V and 30 V, respectively. And the electrode spacing was set as 60 mm and the electrolysis time was 12 h. After 12 hours of operation, the removal rates of Chl-*a* were 22.1%, 50.9%, 70.5% and 95.82 (Fig. 3a), respectively. The corresponding average power were 1.54 W, 2.65 W, 3.88 W and 4.81 W, respectively. The power consumption of per 1% Chl-*a* removal were 0.836 $W \cdot h$, 0.696 $W \cdot h$, 0.652 $W \cdot h$ and 0.602 $W \cdot h$, respectively (Fig. 3b). Thus, the highest inactivation rate of cyanobacteria bloom and efficiency per unit energy consumption was found in the electrode voltage group of 30 V.

The higher the voltage was, the faster the ROS, active chlorine and sulfate radical and other strong oxides were produced during the electrolysis process (Liang et al., 2005; Ghasemian et al., 2017; Bakheet et al., 2018). However,

higher voltage would also lead to the increase of electric current, and excessive energy would be wasted on the electrolysis of water, and the inactivation rate of cyanobacteria bloom would also reduced. Therefore, for get the best efficiency of cyanobacteria bloom removal, the voltage, electrode spacing and electrifying time need to be optimized. The electrode spacing, electrode voltage, and electrolysis time should be considered comprehensively to achieve the optimal balance of the inactivation rate of cyanobacteria bloom and power efficiency.

Figure 3. Change of Chl-*a* concentration in water (a) and energy consumption (b) under different voltage of 15 V, 20 V, 25 V and 30

3.2 Effect of electrolysis on phosphorus removal

The P decomposed after the death of cyanobacteria is one of the key factor why cyanobacteria erupted repeatedly and electrolysis is an method to reduce P in water (Sas et al., 1989; Manso et al., 2000; Gao et al., 2009; Jeon et al., 2014; Bouma-Gregson et al., 2019). In this experiment, during the electrolysis inactivation of cyanobacteria bloom, the TP concentration was continuously reduced after electrolysis of 6 hours. As the P in cyanobacteria bloom was released into the water as DIP was increased. After the electrolysis of 12 hours, the concentration of DIP was increased 76.22% compared with the initial concentration, as the control group dreased 4.76%, but there was a significant difference of TP concentration between these two groups (p 0.001) during electrolysis of 7 hours to 12 hours. The decreased TP in the water may was caused as the cyanobacteria cells die and the organophosphorus in the water was reduced which was decompose into DIP. Thus, the DIP concentration was increased during the initial stage, but after 12 hours of electrolysis, the concentration of DIP in water increased slowly after being electrified and reached the maximum value of 1.84 $\pm$ 0.10 mg/L.

Figure 4 Effect of electrolysis inactivation of cyanobacteria bloom on TP concentration in water (a) and the DTP concentration in vitro and in cyanobacteria (b) as the electrolysis distancing was 60 mm, voltage was 30 V and electrolysis time was 12 h

Electrolysis promoted the P release from cyanobacteria bloom, and promoted the organophosphorus decompose to inorganic P on the anode area since the H^+ was higher and electrodeposition of PO_4^{3-}-P from organophosphorus which enhanced the removal of P in the water. At the same time, the concentration of DIP in the cyanobacteria showed a trend of falling, reduced to 0.18 $\pm$ 0.03 mg/L after 12 hours of electrolysis, and the concentration of DIP in water increased from 1.05 $\pm$ 0.04 mg/L to 1.74 $\pm$ 0.10 mg/L, as there was about 0.69 mg/L DIP was increased in water as about 0.34 mg /L DIP was come from cyanobacteria bloom and we could inferred that mostly DIP was come from decomposed by organophosphorus as the electrolysis enhanced the organophosphorus decomposed to DIP. The change of local pH value caused by electrolysis was the main reason for the decompose of organophosphorus from cyanobacteria to DIP in

water. It could be seen from the Fig. 8a that the pH value near the anode area decreased to 3.5 while the pH value of the cathode area increased to 8.5. The pH value of the control group stabilized at about 6.5.

Figure 5 Effect of electrolysis inactivation of cyanobacteria bloom and the DIP in water (a) and DIP (b) in cyanobacteria as the electrolysis distancing was 60 mm, voltage was 30 V and electrolysis time was 12 h

The main reason for the decrease of TP in water may be that part of P forms insoluble calcium phosphate, struvite and other substances, which precipitate together with calcium carbonate, brucite and other substances (Sun et al., 2020). Due to the high pH value of the cathode, the formation of P chemicals was provided. Finally, white electro-deposited materials were formed on the surface of the cathode. It could be seen that the shape of the electro-deposited material on the Ti cathode surface was irregular (Fig. 6). Some DIP was reduced by electro-deposition on Ti cathode and some DIP was precipitated with Ca^{2+} and Mg^{2+} in water since the concentrations of Ca^{2+} and Mg^{2+} in water was 27.35 mg/L and 5.21 mg/L, respectively. And the other Ca^{2+} and Mg^{2+} was came from the inactivation of cyanobacterial bloom during the electrolysis process since the concentrations of Ca^{2+} and Mg^{2+} in the cyanobacterial bloom of Taihu lake were about 4000 g/g and 1000 g/g, calculated by dry mass (Su et al., 2010). The mass ratio of each element in the electro-deposited material on cathode was analyzed by EDS which was shown in table 2. After the electrolysis inactivation of cyanobacterial bloom, the electro-deposited material cathode was mainly composed of C, O, P, Ca and Mg, and the mass ratio of P is about 0.4%. Under the alkaline condition near the cathode, according to the solubility product of Ca^{2+}, Mg^{2+}, $PO_4{}^{3-}$, $CO_3{}^{2-}$, OH^-, the electro-deposited material may be a mixture of hydroxyapatite, calcium carbonate, calcium magnesium carbonate and so on. With the higher pH the deposition of calcium carbonate was increased as the calcium phosphate was decreased during the electrolysis process (Lei et al., 2018). The higher pH was enhanced the electro-deposition of Ca^{2+}, Mg^{2+}, $PO_4{}^{3-}$, $CO_3{}^{2-}$. After the electrolysis inactivation of cyanobacteria bloom, the ions of Ca^{2+}, Mg^{2+}, $PO_4{}^{3-}$ and $CO_3{}^{2-}$ released during the electrochemical oxidation of cyanobacteria, and the chemical properties of the electrochemical solution on the electrochemical deposition need further study. In addition, it was found out (House et al., 1999) that the electro-deposited material on the cathode surface could reduce the effective area of the electrode and increase the current density. High current density would lead to violent hydrogen evolution reaction on the cathode surface, which is not conducive to the adhesion of calcium phosphate and other deposits. Therefore, it is necessary to remove the electro-deposited material from the cathode timely and regularly.

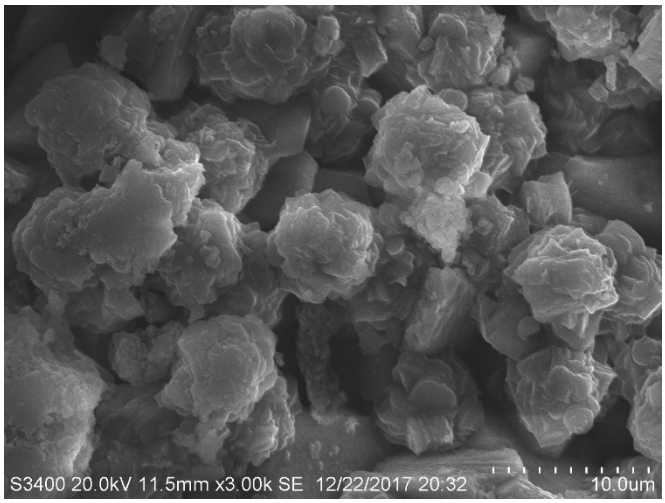

Figure 6 SEM images of electro-deposited material on the Ti cathode at the end of electrolysis

Table 2 Element percentage of electro-deposited material on the Ti cathode

	%
C	43.1
O	38.7
Ca	13.5
Mg	1.3
P	0.4

3.3 Effect of electrolysis on nitrogen removal on water of cyanobacteria bloom

It could be seen from Fig. 7a that the TN concentration of water decreased to a certain extent during the process of electrolysis. After 12 hours of electrolysis, the TN concentration of electrolysis group decreased by 4.58% as the concentration decreased from 43.68 ± 0.12 mg/L to 41.89 ± 0.11 mg/L. Thus, the inactivation effect of electrolysis on cyanobacteria was faster, but the removal ability of nitrogen was limited during the process. The change of NO_3^--N, NO_2^--N concentration was not obvious since the concentration of NO_3^--N, NO_2^--N increased about 8.12% and 3.34%. And RuO_2-IrO_2/Ti mesh anode was effectively for the removal of NH_3-N as in the initial 4 hours the NH_3-N concentration decreased from 18.68 mg/L to 15.4 mg/L, the other was in the process of electrolysis to remove cyanobacteria, the electrolysis reaction had a certain removal effect on NH_3-N as the results was consistent with the removal way of NH_3-N by IrO_2 anode through adsorption and degradation. Oxidation of RuO_2-IrO_2/Ti anode was also another way to remove NH_3-N, since voltam-

metric studies have shown that NH_3-N is more susceptible to oxidation than water (or hydroxide ion), and hence that hydroxide ion can be oxidized in the potential region of water stability (Bunce et al., 2011). In the electrolysis inactivation process of cyanobacteria bloom, with the decomposition of the organic nitrogen in cyanobacteria bloom was transformed into inorganic NH_3-N, resulting in the increase of NH_3-N. As we seen when the chla-*a* was decreased from the concentration of 10.76 ± 0.2 mg/L in initial to 0.58 ± 0.004 mg/L in 10 hours as the death of cyanobacterial cells increased more NH_3-N released and the NH_3-N concentraton increased rapidly to 23.34 ± 0.73 mg/L.

Figure 7 Change of TN (a), NO_2^--N (b), NO_3^--N (c) and NH_3-N (d) concentrations during the electrolysis inactivation of cyanobacteria bloom as the electrolysis distancing was 60 mm, voltage was 30 V and electrolysis time was 12 h

3.4 Effect of electrolysis on water qualities of cyanobacteria bloom

After 12 hours of electrolysis, the pH value near the anode area was decreased to 3.5, and the pH value in the cathode area was increased to 8.5, as the pH value of the control group was stable at about 6.5 (Fig. 8a). The water near the anode was acidic due to the decomposition of cyanobacteria and a large amount of H^+ was produced by electrolytic water reaction; the water near the cathode was alkaline due to the large amount of OH^- released by electrolytic water reaction since the water could electrolyized when the theoretical voltage was more than 1.23 V. The Körbahti found that low pH conditions can promote the production of $\cdot OH$ and other strong oxidizing substances, and the degradation efficiency of organic compounds would be significantly improved (Körbahti et al., 2003). Therefore, the inactivation of cyanobacteria bloom could be improved when the anode area keeping an acid condition during the electrolysis prcess.

Compared with the control group, the ORP near the anode increased with the increase of electrolysis time, increased from 172.6 ± 4.52 mV to 233.7 ± 4.75 mV, with an increase rate of 35.4%; while the ORP near the cathode decreased slightly to 153.90 ± 3.45 mV after 12 hours reaction (Fig. 8b), indicating that the accumulation of strong oxidizing substances in the water near the anode such as O_3, H_2O_2 and $\cdot OH$ were produced near the anode since the voltage was 15 V due to electrolytic water reaction, which effectively oxidized organic matters such as proteins and sugars released from cyanobacteria cell, which was one of the main reasons for damaging cyanobacterial cells (Jeon et al., 2014; Ghasemian et al., 2017).

The DO in the water near the anode kept increasing gradually after electrolysis treatment, until 12 hours after being electrified, the DO concentration in water increased by 63.2% (Fig. 8c). During the death of cyanobacteria large numer of DO was depledted which brought about a sharp deterioration of DO (Zhang et al., 2010). As the DO near the cathode decreased by 46.6%, moreover, the

cathode area can not be rapily supplemented by oxygen produced by electrolysis water reaction, and the cathode area forms an envirnoment of low DO. With the destruction of cyanobacterial cells and the outflow of cytoplasm, the electrical conductivity of water body increased, and the current intensity in water also increased, resulting more oxygen produced due to the increase of reaction speed of electrolytic water and the rising speed of DO gradually increased.

After being electrified for 12 hours, the salinity of electrolysis group increased from 0.23 ‰ to 0.43 ‰, increased by 95.5%; while that of control group increased from 0.22 ‰ to 0.28 ‰ (Fig. 8c). In the electrolysis process of inactivation of cyanobacteria bloom a large amount of soluble salts were released into the water body, which made the salinity of water increased, the conductivity increased, and the reaction current also increased under the condition of constant applied voltage (Figure S2). The increased current which further accelerated the ability to electrolyze water.

Figure 8 The change of pH, ORP, DO and salt during the inactivation of cyanobacteria bloom by electrolysis as the electrolysis distancing was 60 mm, voltage was 30 V and electrolysis time was 12 h

4 Conclusions

(1) Voltage, electrode spacing and electrolysis time were the main factors influencing the current size and energy consumption by electrolysis. The order of influence of each factor on theoretical energy consumption of algaecide was electrode spacing > electrode voltage > electrolysis time through the orthogonal test method. Considering the energy consumption, the electrode spacing of 60 mm, electrode voltage was 30 V and electrolysis time was 12 hours were the most appropriate factors to removal cyanobacteria bloom.

(2) The strong acidic environment produced by electrolysis also promoted the transformation of organophosphorus to inorganic phosphorus. DIP, Ca^{2+} and Mg^{2+} ions in water were reduced through chemically precipitated, and deposited to Ti cathode in alkaline environment of cathode. Electrolysis also promoted the transformation and partial removal of phosphorus.

(3) Electrolysis enhanced the removal of NH_3-N through direct and indirect oxidation by Ti anode and have a certain ability to remove nitrogen.

(4) The lower pH conditions could promote the production of $\cdot OH$ and other strong oxidizing substances which was the main reason to the inactivation of cyanobacteria bloom, in the alkaline environment near the cathode enhanced the electro-deposition of Ca^{2+}, Mg^{2+}, ${PO_4}^{3-}$, ${CO_3}^{2-}$. The accumulation of strong oxidizing substances in the water near the anode such as O_3, H_2O_2 and $\cdot OH$ were produced due to electrolytic water reaction. The salinity of electrolysis group increased from 0.23 ‰ to 0.43 ‰ and promoted the formation of free radicals. The high DO concentration was beneficial to aerobic removal of nitrogen released by cyanobacteria bloom.

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