Study on mechanism of algal inactivation and pollution removal by Fe-ACF electro Fenton-like process

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ABSTRACT

Algae inactivation and algal metabolic pollutant removal of *Chlorella* and *Duneliella salina* from seawater by the Fe-ACF electro Fenton-like process has been studied. The experiments were conducted at neutral condition of pH 8.3 (raw water) and 6.2 to break through the limit of strong acidic conditions. Experimental results indicated that the Fe-ACF electro Fenton-like process has a good effect for algae inactivation and for pollutant removal in neutral conditions, and pH has no obvious effect for the inactivation of algae. At optimum conditions, the inactivation efficiency for algae could reach up to 98%. A pH of 8.3 is more favorable for pollutant removal. Under neutral pH conditions, the coupling effect of indirect oxidation of •OH, direct oxidation of free chlorine and coagulation and adsorption of ferric and ferrous hydroxy complexes in the electro Fenton-like process was achieved, and the coupling effect promotes the inactivation of algae and the removal of metabolic pollutants.

Key words | algae inactivation, coagulation and adsorption, direct oxidation, electro Fenton-like, indirection oxidation, metabolic pollutants

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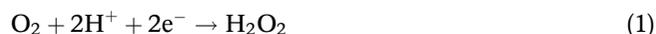Dalian Maritime University,
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INTRODUCTION

In recent years, the electro-Fenton technique has been studied extensively for organic pollutant destruction in water, and has achieved preferable development (Scialdone *et al.* 2013; El-Hanafi *et al.* 2014; Bounab *et al.* 2015). The electro-Fenton process has been shown to be an effective alternative for the removal of several organic compounds, especially refractory organic compounds and so on (Fernández de Dios *et al.* 2014; Marco *et al.* 2014). Electro-Fenton is mainly relied upon *in situ* and for catalytic production of Fenton's reagents, a mixture of hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}), to produce hydroxyl radicals to react with organic pollutants in water, finally leading to their destruction (Reactions (1)–(3)) (Pozzo *et al.* 2005; Papi *et al.* 2009; Wang *et al.* 2014; Olvera-Vargas et al. 2014), The main advantage of the electro-Fenton process was its characteristics of cathodic regeneration of Fe^{2+} and continuous *in-situ* generation of H_2O_2 in an acidic medium.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \bullet OH \tag{2}$$

$$Fe^{3+} + e^- + \bullet OH \rightarrow Fe^{2+} \tag{3}$$

Traditionally, the electro-Fenton process refers to the advanced oxidation of hydrogen radicals by electrolysis at strong acidic conditions (pH 1–3) (Sires & Brillas 2012; Chen & Huang 2012; Sahinkaya 2013). The narrow working pH range limits the wide use of the electro-Fenton process (Li *et al.* 2009; Wang *et al.* 2010; Zhang *et al.* 2015). In this preliminary study, the Fe-ACF electro Fenton-like process was conducted at neutral pH to break through the limit of strong acidic conditions.

Algae metabolites, such as algae toxins, cause serious water pollution (Huang *et al.* 2008; Laabir *et al.* 2012; Vichi *et al.* 2012). The objective of our study was to reflect the mechanism of inactivation of algae and pollutant removal by an electro Fenton-like process. In the study, *Chlorella* and *Dunaliella salina* were selected as the representative algae. To break through the limitation of strong acidic conditions, the Fe-ACF electro Fenton-like process was conducted at a neutral pH range.

MATERIALS AND METHODS

Electro Fenton-like setup and characterization

The electro Fenton-like setup used here is shown in Figure 1. Batch mode experiments were conducted in an undivided
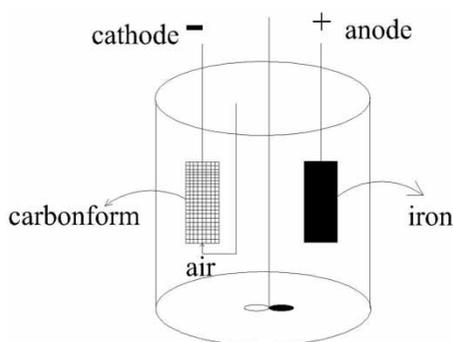
Figure 1 | The experiment setup used in this work.

glass cell under vigorous stirring performed by a magnetic stirrer with 1,000 mL of solution, equipped with an air pump, a DC power supply and a conductivity/pH meter. The applied potential and temperature were optimized in the range of 1–6 V and room temperature, respectively.

The anode was a sheet of iron sized 10 cm × 10 cm × 0.2 cm, and the cathode was an activated carbon fiber sized 10 cm × 10 cm × 0.2 cm, and the distance between anode and cathode was 5 cm. Compressed air was fed to the cathode by an air pump at 250 mL/min for 5 min before the power was on, and was maintained during the process of electrolysis.

Chlorella and *Dunaliella salina* were cultured in seawater.

The pH was an important factor in water. Although pH less than 5 would be favored for the production of ·OH in the electro-Fenton process, pH less than 5 or greater than 9 would affect the viability of algae in water. In the study, the pH of the water was selected at 8.3 (initial pH of raw water) and 6.2 (adjusted by addition of solution of 0.1 mol/L sulfuric acid and sodium hydroxide). The two different pH values were near neutral and were in the common pH range of natural water, and the pH does not affect the viability of the algae.

Analytical methods

The concentration of the algae was analyzed by microscope counting and optical density of OD_{685} synchronously. The method of microscope counting to express the content of algae in water is simple and intuitive, but there is a risk of human error. Optical density of OD_{685} can be used to present the density of algae, but it lacks accuracy. The concentration of pollution was analyzed by UV_{254} (absorbance at 254 nm) (Ng *et al.* 2012; Gerrity *et al.* 2012; Yu *et al.* 2014; Li *et al.* 2015a, b) and COD_{Mn} (potassium permanganate index) (Wu *et al.* 1987; Pei *et al.* 2007; Khorsandi *et al.* 2014; Jiao *et al.* 2015; Li *et al.* 2015a, b). The COD_{Mn} concentration analysis referred to standard methods (EPAC 2002). Free residue

chlorine, Cl^-, Fe^{2+} and Fe^{3+} were analysed by chemical methods. Hydrogen radicals were trapped with dimethyl sulfoxide and quantified by high performance liquid chromatography (HPLC) (Tai *et al.* 2004). The evaluation was carried out with a reversed-phase Nucleodur C18 Column (250 mm × 4.6 mm, 5 μm) and UV-visible detector (Agilent 1200 DAD) at 275 nm. The mobile phase was methanol/water (55:45%), with a flow rate of 1 mL/min and temperature of 23 °C. Both solvents were previously filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter and degassed ultrasonically. The pH was measured using a pH meter.

The removal rate of algae and pollutants were calculated by the following equation:

$$R = \frac{C_0 - C}{C_0} \times 100\% \tag{4}$$

where C_0 is the initial concentration, C is the final concentration.

The specific energy consumption (EC) of pollutant removal (take chemical oxygen demand (COD) as representative) was calculated by the following equation (Ammar *et al.* 2015):

$$EC\left(kWh(gCOD)^{-1}\right) = \frac{1,000 \times UIt}{\Delta C \times V} \tag{5}$$

where U is the applied potential (V), I is the current (A), t is the electrolysis time (h), ΔC is the change in COD concentration, V is the solution volume (L).

Experimental procedures

Laboratory-scale experiments were carried out with DC conditions power supply. The volume of water was 1,000 mL. The pH was adjusted with a solution of 0.1 mol/L sulfuric acid and sodium hydroxide. The cell voltage varied from 1–6 V, the current density applied ranged from 0.5–5 mA/cm². At certain time intervals, samples of 20 mL volume were taken from the solution and filtered through 0.20 μm Nylon filters and analyzed for OD_{685}, COD, and UV_{254}.

RESULTS AND DISCUSSION

Inactivation effects for *Chlorella* and *Dunaliella salina*

The inactivation effects for *Chlorella* and *Dunaliella salina* are shown in Figures 2 and 3. The inactivation efficiency
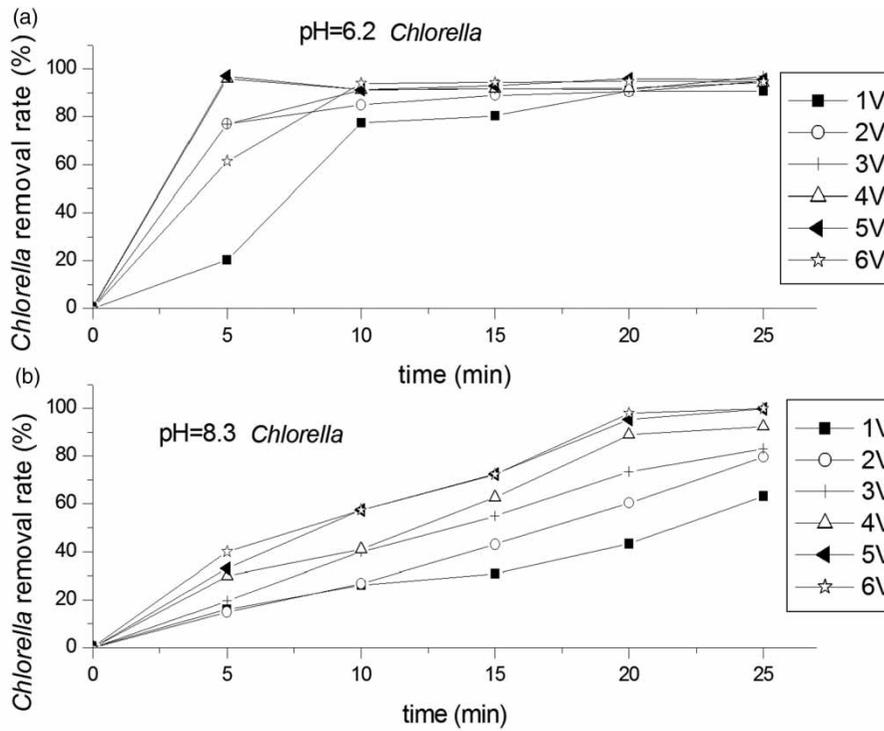
Figure 2 | Inactivation efficiency for *Chlorella*; (a) is conducted at pH of 6.2 and (b) is at pH of 8.3. The voltage changed from 1 V to 6 V. Algae concentration was analyzed by microscope counting.
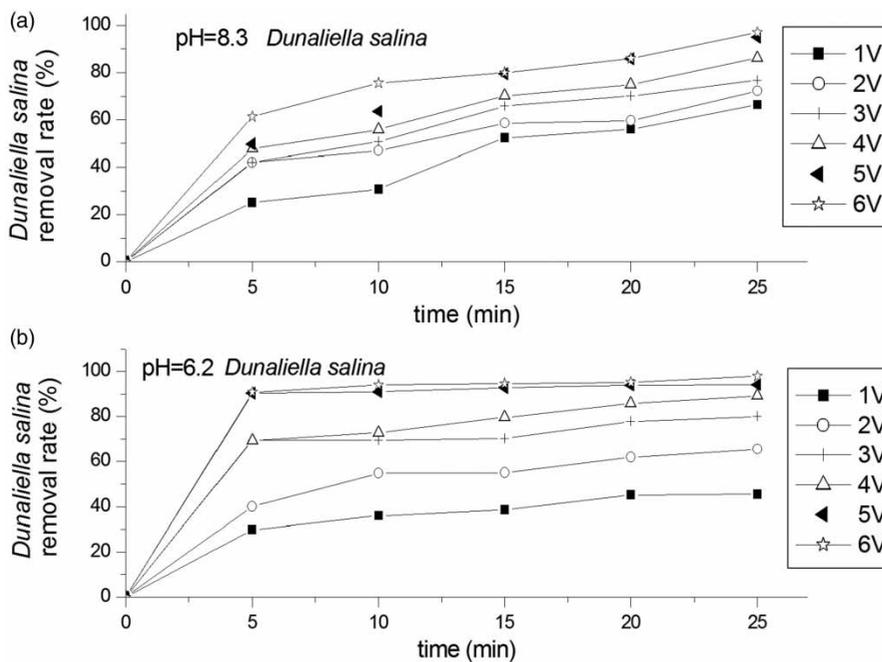

Figure 3 | Inactivation efficiency for *Dunaliella salina*; (a) is conducted at pH of 8.3 and (b) is at pH of 6.2. The voltage changed from 1 V to 6 V. Algae concentration was analyzed by microscope counting.

was calculated by Equation (4), and the number of algae was expressed by microscopic counting.

The results in Figures 2 and 3 show that the inactivation rate for algae increased with the increase of voltage. From the inactivation for *Chlorella* at a pH of 8.3 in Figure 2(a), it could be seen that the inactivation efficiency increased to 99.4% in 25 min at a voltage of 6 V. In Figure 2(b) at a pH of 6.2, the inactivation efficiency reached 97.9% in 25 min at a voltage of 3 V. These results showed that the ACF-Fe electro Fenton-like process has high inactivation efficiency for *Chlorella* under neutral pH conditions and the inactivation effect at pH 6.2 was a little better.

Figure 3 shows the inactivation effect for *Dunaliella salina*. The results showed that the inactivation effect for *Dunaliella salina* increased with the increase of voltage and electrolysis time.

At a natural pH of 8.3, the inactivation efficiency reached to 46.3% in 25 min at a voltage of 1 V, and increased to 97.2% at a voltage of 6 V. At a pH of 6.2, the inactivation efficiency was 66.7% in 25 min at a voltage of 1 V, and increased to 97.5% at a voltage of 6 V. These results showed that the Fe-ACF electro Fenton-like process was effective for *Dunaliella salina* inactivation.

OD_{685} was used to express the algae density in water. Figures 4 and 5 show the effects on the change of the optical density of OD_{685}.

The results in Figures 4 and 5 show that the optical density of OD_{685} reduced with increasing voltage during the electrolysis process, and there was no obvious difference between pH 8.3 and 6.2. The results of optical density were consistent with that of microscope counting. The methods of optical density and microscope counting for algae analysis were actually feasible.

Removal efficiency for UV_{254}

UV_{254} was used to express the relative contents of organic matters that have conjugated π-ponds and so on. Usually, UV_{254} is used to represent the relative organic pollution degree of water. The removal efficiency for UV_{254} in the process was shown in Figures 6 (*Chlorella*) and 7 (*Dunaliella salina*).

From Figures 6 and 7, it can be seen that the Fe-ACF electro Fenton-like process has some effect on removal for UV_{254}. In Figure 6, when pH was 8.3, the removal effect for UV_{254} increased with the increase of voltage. When the voltage was 1 V, the removal efficiency for UV_{254} was small. But when the voltage was 6 V, the UV_{254} decreased from 0.324 to 0.001 in 25 min, and the removal efficiency was 99.7%. At pH 6.2, the removal efficiency for UV_{254} was smaller than that at pH of 8.3, and
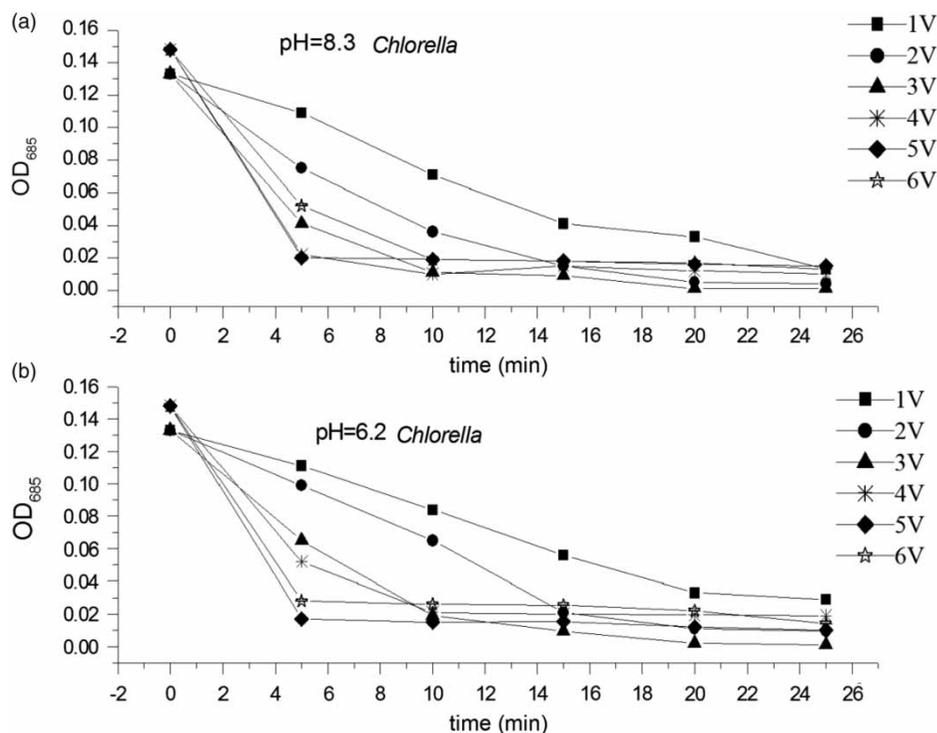

Figure 4 | The effect for OD_{685} of *Chlorella*; (a) is conducted at pH of 8.3 and (b) is at pH of 6.2. The voltage changed from 1 V to 6 V.
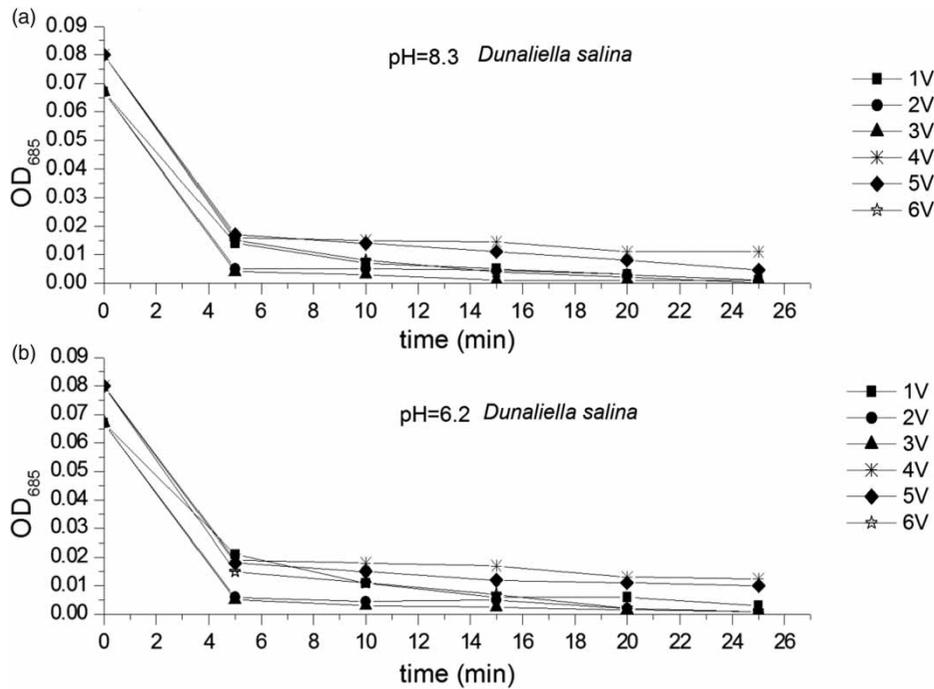
Figure 5 │ The effect for OD_{685} of *Dunaliella salina*; (a) is conducted at pH of 8.3 and (b) is at pH of 6.2. The voltage changed from 1 to 6 V.
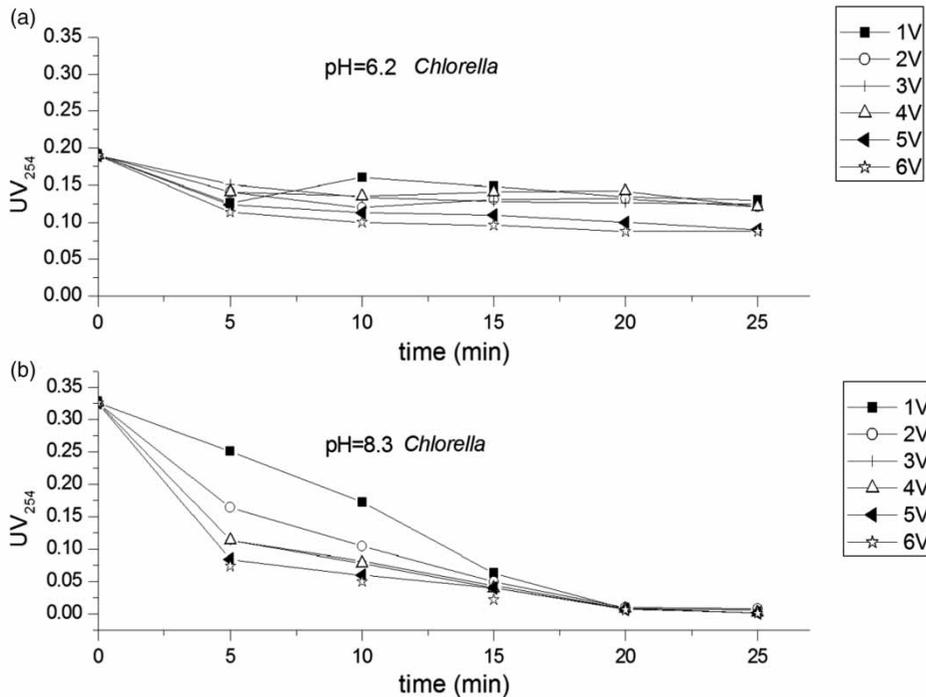

Figure 6 │ Removal effect for UV_{254} of *Chlorella*; (a) is conducted at pH of 6.2 and (b) is at pH of 8.3. The voltage changed from 1 V to 6 V.

the removal efficiency was 53.4% at 6 V in 25 min. These results showed that a pH of 8.3 was advantageous for the removal for UV_{254}.

In Figure 7, the results were the same as in Figure 6. The process has effects for the removal of UV_{254}, and at pH 8.3, the removal effect was a little higher than at pH 6.2.
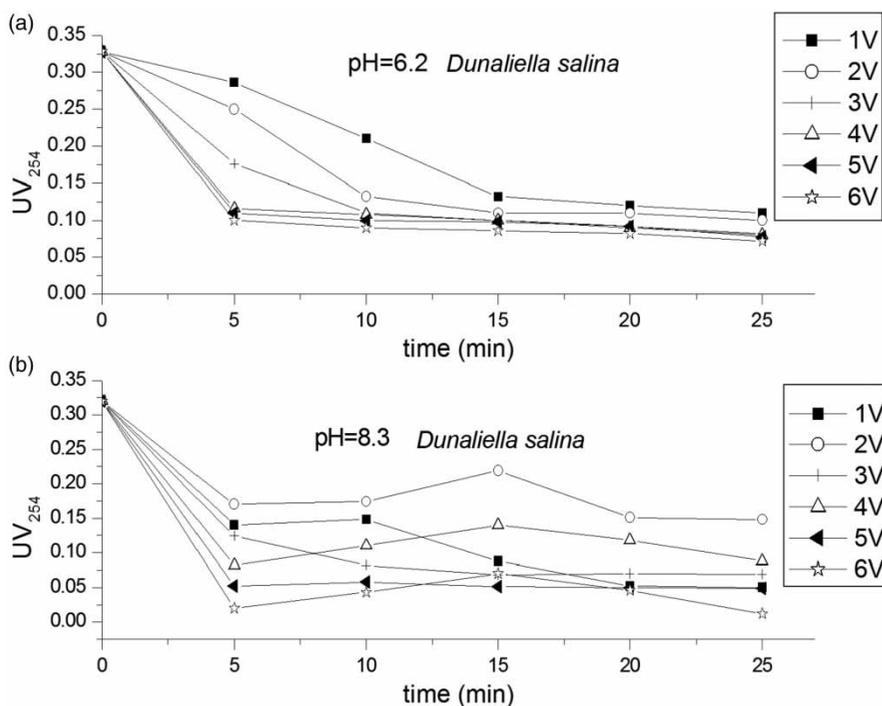
Figure 7 │ Removal effect for UV$_{254}$ of *Dunaliella salina*; (a) is conducted at pH of 6.2 and (b) is at pH of 8.3. The voltage changed from 1 V to 6 V.

Removal efficiency for COD$_{Mn}$

COD$_{Mn}$ is used to express the relative content of substances that can be oxidized in water. In the study, the concentration of COD$_{Mn}$ was used to present the contaminants of algae metabolites. Figures 8 and 9 show the removal results for COD$_{Mn}$.

It can be seen that COD$_{Mn}$ decreased in some extents during the electro Fenton-like process, and the removal effects increased with the increase of operational voltage.

For *Chlorella*, at a pH of 8.3, the removal efficiency for COD$_{Mn}$ increased from 75.7% at 1 V in 25 min to 98.5% at 6 V in 25 min. At a pH of 6.2, the COD$_{Mn}$ removal efficiency increased from 22.7% at 1 V in 25 min to 65.8% at 6 V in 25 min.

For *Dunaliella salina*, which was the same as *Chlorella*, the removal efficiency for COD$_{Mn}$ could increase up to 81.3% and 82.8% at a pH of 8.3 and 6.2.

COD$_{Mn}$ expresses the relative content of organic matter in water. The results of COD$_{Mn}$ removal showed that the Fe-ACF electro Fenton-like process has higher removal capacity for organic pollutants produced by algae.

The EC$_{COD}$ of the above trials calculated from Equation (12) *vs.* the percentage of COD$_{Mn}$ removal during the electro Fenton-like treatments was analyzed. In the process, the voltage was between 1–6 V, I was 0.1–1 A, and *t* was about 0.5 h. Then the EC was calculated, which was $0.1–0.3/(kWh(g\ COD^{-1}))$.

Mechanism analysis for algae inactivation and pollutants removal

As one of advanced oxidation process, electro-Fenton technology has been used widely in organic pollutants degradation in water. In this study, the electrolysis was conducted under neutral conditions to break through the limit of strong acidic pH condition. The study results showed that the Fe-ACF electro Fenton-like process has a high efficiency for algae inactivation and pollution removal.

Felix-Navarro *et al.* (2011) have shown that in the process of electrolysis, there has been coexistence of indirect oxidation of ·OH and direct oxidation of other oxidants, and Bedoui *et al.* (2009) have shown the multi function of direct oxidation, indirect oxidation of ·OH and other oxidation of $S_2O_8^{2-}$ and SO_5^{2-} and so on.

In this study, iron and ACF were used as the anode and cathode, respectively, in the electro Fenton-like system in seawater with a high concentration of Cl$^-$ at neutral pH conditions. Although under neutral conditions, the production of ·OH is not very high, but the iron anode would be oxidized to Fe^{2+} and Fe^{3+} and then form ferric and ferrous hydrous compounds through
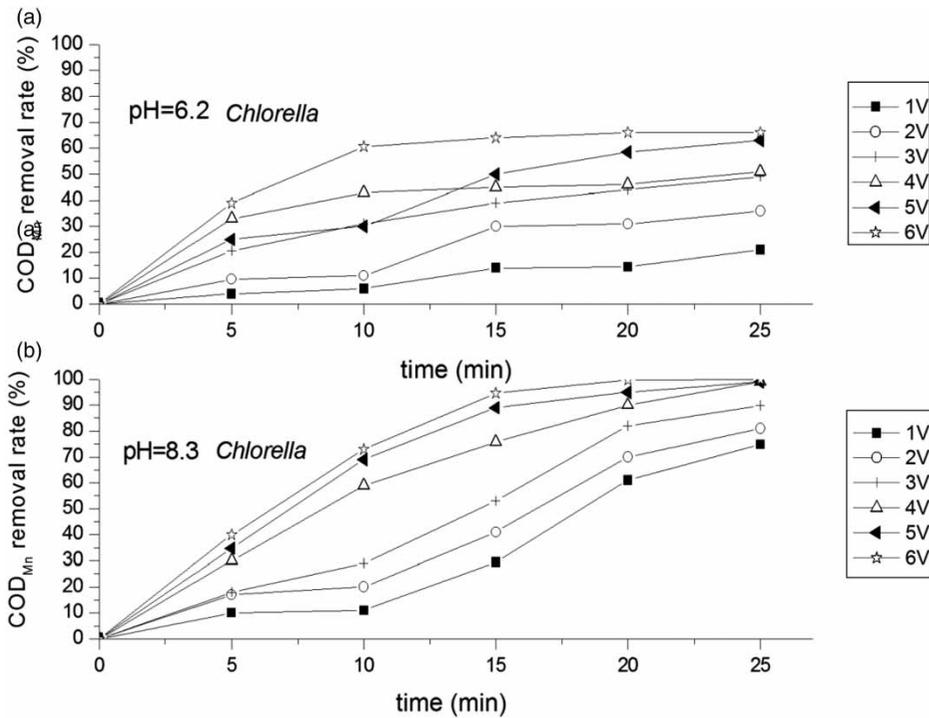
Figure 8 │ Removal effect for COD_{Mn} of *Chlorella*; (a) is at pH condition of 6.2 and (b) is of 8.3. The voltage changed from 1 V to 6 V. The initial concentration of COD_{Mn} is 12.27 mg/L.
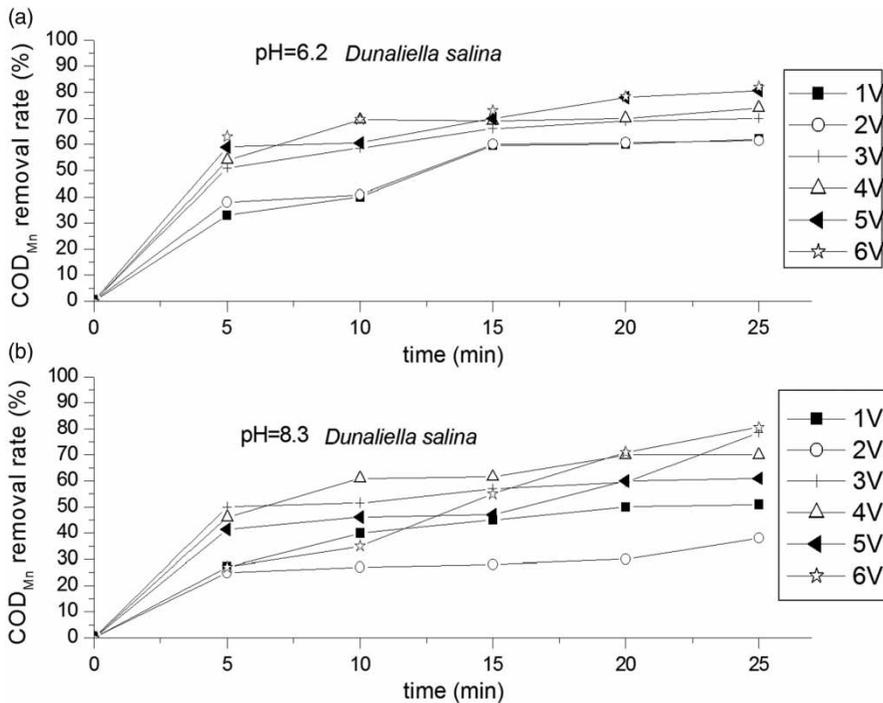

Figure 9 │ Removal effect for COD_{Mn} of *Dunaliella salina*; (a) is at pH condition of 6.2 and (b) is of 8.3. The voltage changed from 1 to 6 V. The initial concentration of COD_{Mn} is 11.64 mg/L.

hydrolysis, which would help the removal of algae by coagulation. On the other hand, because of the high reactivity of Cl^-, large amounts of Cl^- in seawater would be oxidized to free chlorine, which would take a role in the inactivation of algae and pollutant removal. In order to clarify the mechanism of algae inactivation and

pollutant removal, the intermediate products of •OH, free chlorine and Fe^{2+} and Fe^{3+} were analyzed.

Analysis of •OH

The •OH concentration was analyzed by HPLC. In the process of electrolysis, the change of •OH concentration is shown in Figure 10.

The •OH was produced in the process of electrolysis. At a pH of 8.3, the concentration of •OH increased with the increase of operation voltage from 1 V to 4 V, while it decreased at 5 V and 6 V, and the concentration of •OH increased at the beginning and then decreased. At a pH of 6.2, the concentration of •OH did not increase to the same as that at pH 8.3. At a voltage of 1 V, 2 V and 6 V, the concentration of •OH was high relatively, but lower at 3 V, 4 V and 5 V. Compared with that of pH 8.3, the concentration of •OH was higher at pH 6.2, which shows that weak acid conditions are favored for the production of •OH.

In the Fe-ACF electro Fenton-like system, Fe^{2+} and H_2O_2 would be produced in the anode and cathode respectively, and then react with each other to produce •OH. When the operational voltage was low, the electrolysis in the two poles increased with the increase of voltage, and the production of •OH increased. But, when the voltage was high enough, the concentration polarization of the electrodes

increased, thus the intermediate products and the reaction between Fe^{2+} and H_2O_2 decreased, and then the production of •OH decreased.

From Figure 10, it can be seen that the curves of ·OH concentration change almost oppositely under pH of 6.2 and 8.3. In this study, experiments were conducted on seawater with a high concentration of Cl^-. Under alkaline conditions of pH 8.3, the small amount of •OH produced would be consumed by Cl^-, ClO_2^- and so on (seen in Equations (5)–(9)), so the curves of •OH concentration change almost oppositely under pH of 6.2 and 8.3.

Analysis results of free chlorine

During the process of electrolysis, Cl^- in water would be oxidized to chlorine and hypochlorite, which would take roles in the oxidation in pollutant removal from water. The production and change of free chlorine was analyzed to clarify the role of free chlorine in algae inactivation and pollutant removal. The change result of free chlorine is shown in Figure 11, and the change of Cl^- is shown in Figure 12.

From the results in Figure 11, it can be seen that there was free chlorine generated in the process of electrolysis, and the concentration of free chlorine increased with the increase of operational voltage to some extent, but it decreased when the voltage increased to a higher value. At
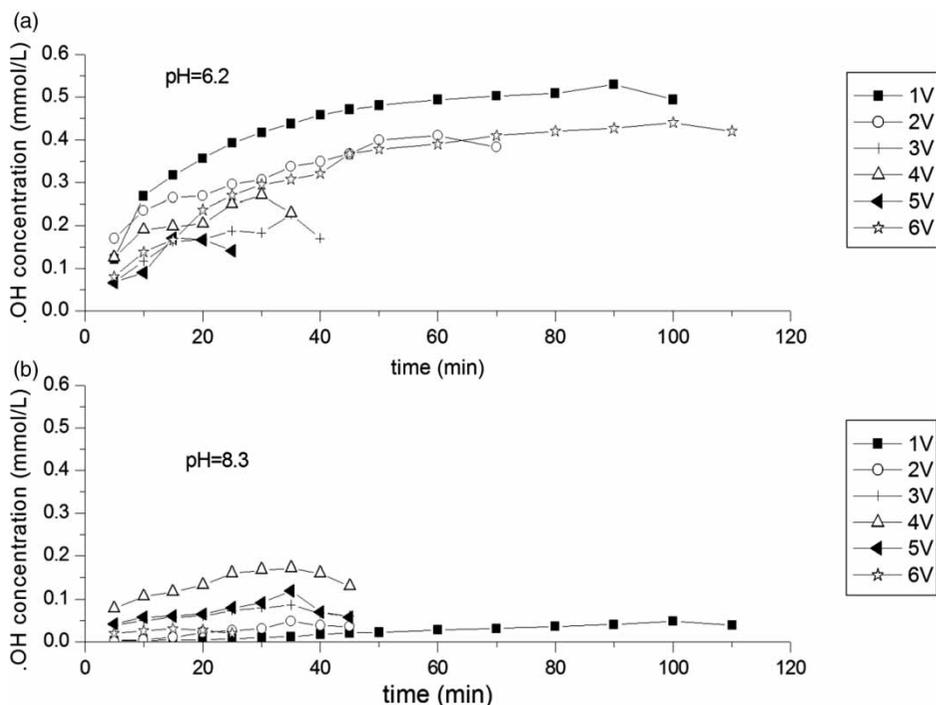

Figure 10 | Change of •OH concentration at different voltages; (a) is at pH condition of 6.2 and (b) is of 8.3. The voltage changed from 1 to 6 V.
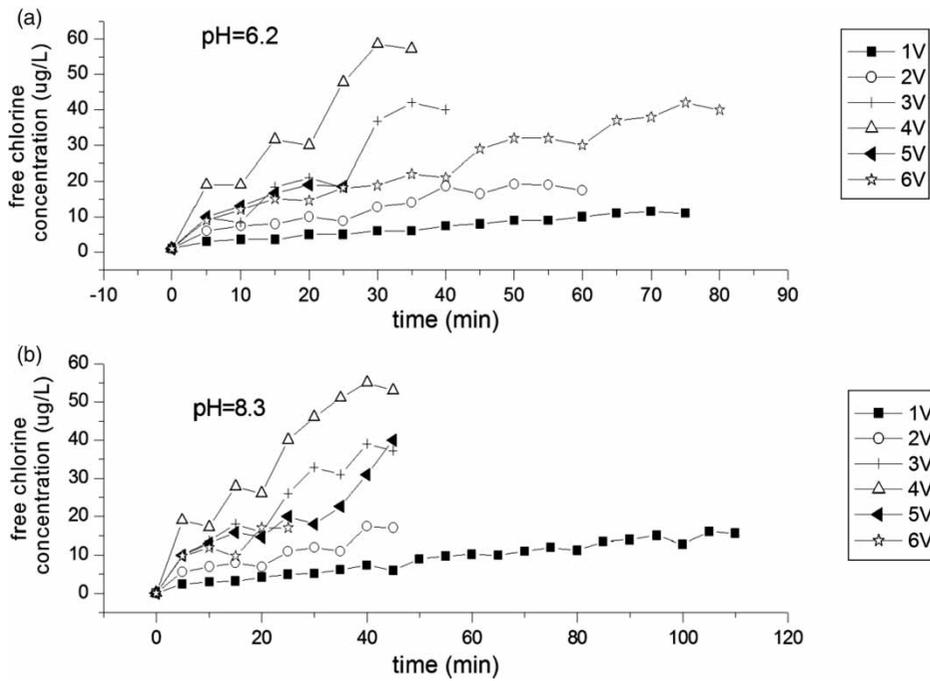
Figure 11 │ Change of free chlorine concentration at different voltage; (a) is at pH condition of 6.2 and (b) is of 8.3. The voltage changed from 1 V to 6 V.
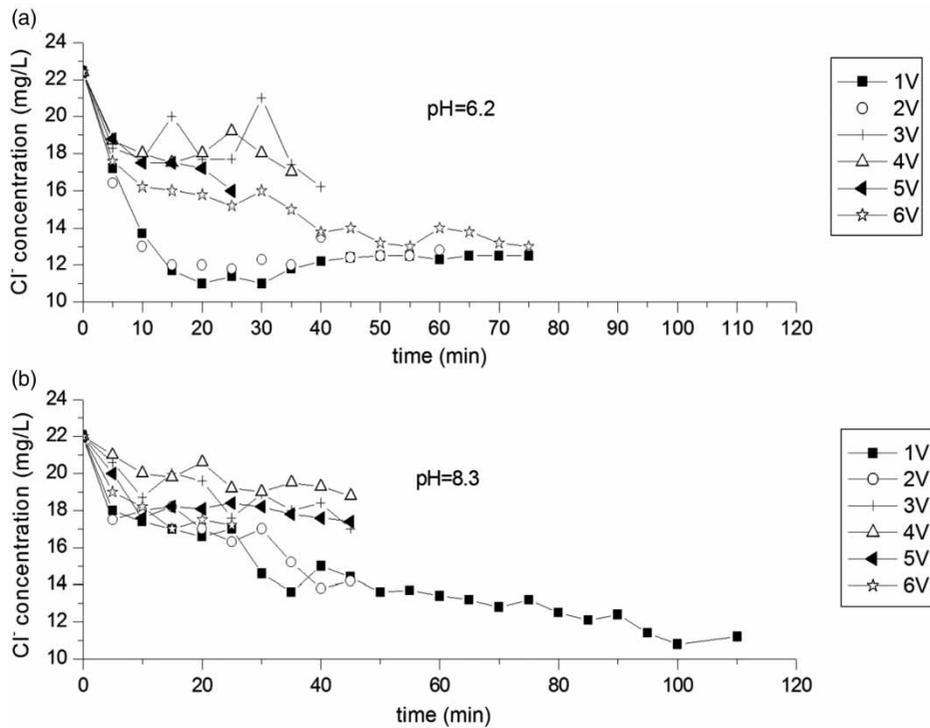

Figure 12 │ Change of Cl⁻ concentration at different voltage; (a) is at pH of 6.2 and (b) is of 8.3. The voltage changed from 1 V to 6 V.
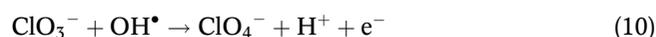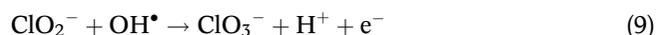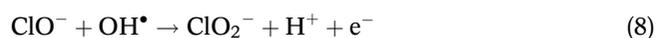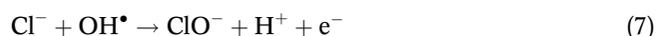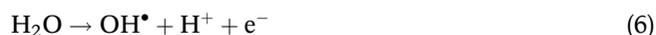
the same time, the concentration change trend of free chlorine at the studied pH values is essentially the same.

The change of Cl^- concentration in Figure 12 showed that the concentration of Cl^- decreased in the process of

electrolysis, which was confirmed with the change trend of free chlorine.

In the electro Fenton-like process, there were effects of chlorine or hypochloric acid, and the effects of free chlorine did not vary with pH values.

From Figures 11 and 12, it can be seen that the concentration of free chlorine increased with the decreased concentration of Cl^-, and both decreased with the abatement of voltage. This may be because the concentration of Cl^- in the water is high, and there would be more Cl^- absorbed in the anode. At lower voltage, Cl^- in anode would be oxidized firstly, and they are almost removed at the conclusion of electrolysis, being completely transformed into hypochlorite (ClO^-), and even chlorate (ClO_3^-), and perchlorates (ClO_4^-) (Dbira *et al.* 2015). These chlorate and perchlorates cannot be analysed by the analysis method for free chlorine, so both free chlorine concentration and Cl^- concentration decreased synchronously.

$$H_2O \rightarrow OH^\bullet + H^+ + e^- \tag{6}$$

$$Cl^- + OH^\bullet \rightarrow ClO^- + H^+ + e^- \tag{7}$$

$$ClO^- + OH^\bullet \rightarrow ClO_2^- + H^+ + e^- \tag{8}$$

$$ClO_2^- + OH^\bullet \rightarrow ClO_3^- + H^+ + e^- \tag{9}$$

$$ClO_3^- + OH^\bullet \rightarrow ClO_4^- + H^+ + e^- \tag{10}$$

The occurrence of chlorate and perchlorate is undesirable and becomes the main drawback in application of electrochemical technology.

Analysis results of Fe^{2+} and Fe^{3+}

In the electrolysis, the Fe anode would be oxidized to Fe^{2+}, which would react with H_2O_2, generated in the cathode, to produce $\bullet OH$. In the process of electrolysis, some Fe^{2+} produced in the anode was unable to react with H_2O_2 and would be oxidized to Fe^{3+}, which would reduce the generation rate of $\bullet OH$, and in neutral pH condition, Fe^{3+} would form ferric hydroxide, etc. with the effects of coagulation and adsorption, and which would agglomerate algae cells and adsorb pollutants in water, and contribute to the removal for algae and pollution. Figures 13 and 14 show the results of the concentration change of Fe^{2+} and Fe^{3+} in the process.

At low voltage of 1 V and 2 V, there was no Fe^{2+} accumulation in 25 min. But with the increase of voltage, there was more and more Fe^{2+} accumulation. This is because at low voltage, the amount of Fe^{2+} generated in the anode was small, and the Fe^{2+} would be consumed by H_2O_2 quickly, so there was no Fe^{2+} accumulation. With the increase of voltage, more and more Fe^{2+} was produced in the anode, but due to
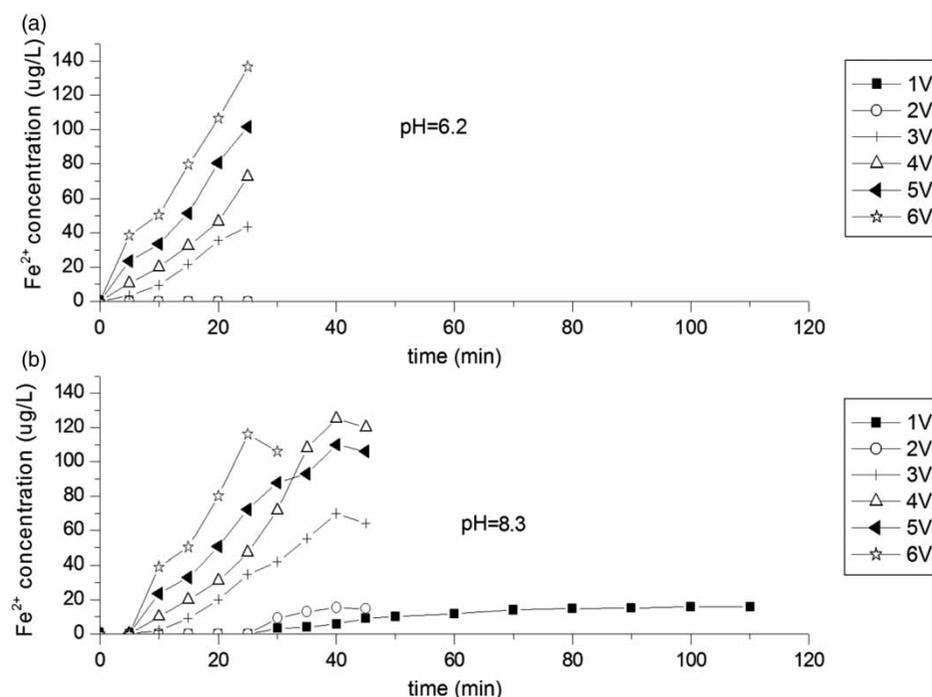

Figure 13 | Change of Fe^{2+} concentration at different voltage; (a) is at pH condition of 6.2 and (b) is of 8.3. The voltage changed from 1 V to 6 V.

Figure 14 │ Change of Fe^{3+} concentration at different voltage; (a) is at pH condition of 6.2 and (b) is of 8.3. The voltage changed from 1 V to 6 V.
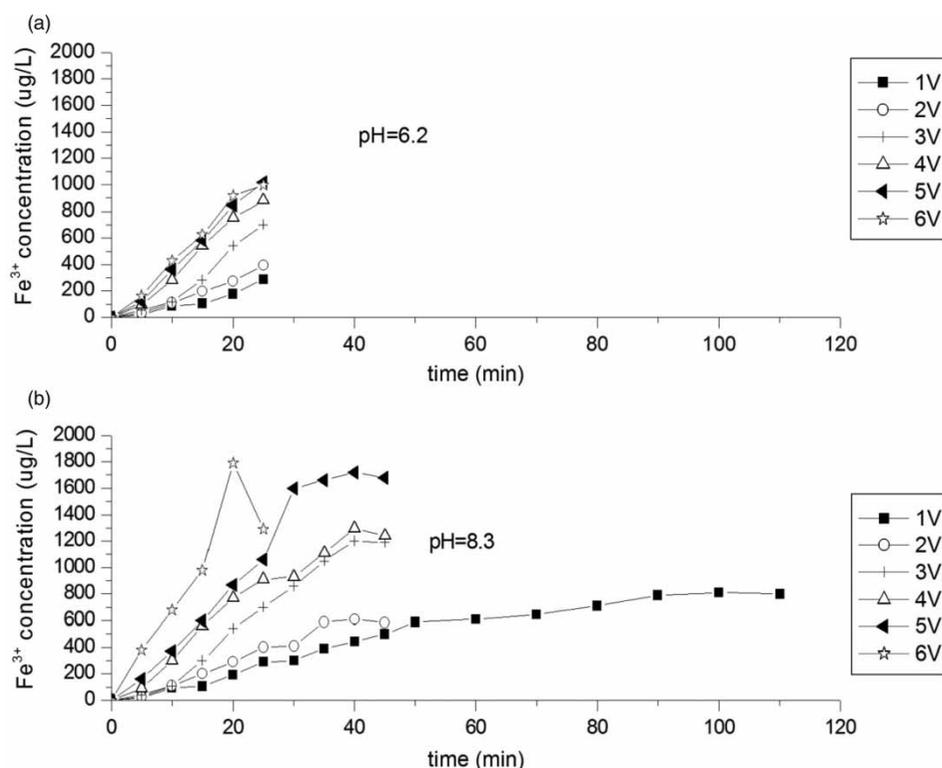
limitations such as mass transfer rate, etc., the increasing Fe^{2+} cannot react with H_2O_2 in the cathode, and results in the accumulation of Fe^{2+}. But, conversely, Fe^{2+} is not stable, and finally it would be consumed by O_2. So, the total concentration of Fe^{2+} was low.

The change of Fe^{3+} concentration was the same as that of Fe^{2+}, which showed that with the accumulation of Fe^{2+}, more and more Fe^{3+} accumulated. In neutral conditions, Fe^{3+} would hydrolyze to ferric hydroxide gradually, which would affect agglomeration and adsorption on removal of algae and some pollutants.

Mechanism of the Fe-ACF electro Fenton-like process

The analysis results showed that $\cdot OH$, Fe^{2+}, Fe^{3+} and free chlorine coexist with certain regularity in the electro Fenton-like process.

The production of $\cdot OH$ increased with the increase of voltage. When the voltage increased to a higher level, the production of $\cdot OH$ decreased. At a certain voltage, the production of $\cdot OH$ increased to the highest point, then declined gradually. A pH of 6.2 is favorable for the production of $\cdot OH$.

The production of free chlorine has no obvious differences at the two pH values.

At low voltage, there was no accumulation of Fe^{2+}. However, with the increase of voltage, more and more of Fe^{2+} was accumulated in the solution.

In the process of electrolysis, there was an accumulation of Fe^{3+}, and the production of Fe^{3+} increased with the increase of voltage.

In the process of the Fe-ACF electro Fenton-like process, Fe^{2+} and H_2O_2 were produced in the anode and cathode, respectively, and then reacted to each other to produce $\cdot OH$.

During a shorter period of electrolysis, the Fe^{2+} generated in the anode reacted with H_2O_2 in the cathode to produce $\cdot OH$, so there was no accumulation of Fe^{2+}, and the production of $\cdot OH$ increased. During a longer period of electrolysis, more and more Fe^{2+} was accumulated in the solution, and the concentration of Fe^{3+} increased. In the study condition of neutral pH, Fe^{3+} would gradually hydrolyze into hydroxide complexes.

At the same time, the amount of Cl^- in water has been electro-oxidized to free chlorine, such as chlorine and hypochlorite. The reactions are expressed as follows ((11)–(13)) (Panizza *et al.* 2000):

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{11}$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- \tag{12}$$

$$HOCl \rightarrow H + OCl^- \tag{13}$$

To sum up, it could be concluded that in the process of algae and pollution removal by an electro Fenton-like process, there were effects of indirect oxidation of ·OH, coagulation and adsorption of ferric and ferrous hydroxide complexes, and direct oxidation of free chlorine, etc. The synergistic coupling effect of these factors implements the removal of algae and organic pollution.

Under optimum experimental conditions, the Fe-ACF electro Fenton-like system could break through the limit of the single constraint of advanced oxidation of ·OH at acidic conditions. The coupling effects of different factors achieved higher removal efficiency for pollution.

CONCLUSIONS

This study has focused on inactivation of *Chlorella* and *Dunaliella salina* using an Fe-ACF electro Fenton-like process, and the mechanism for algae inactivation and pollution removal was clarified.

The process has a high effect on inactivation for *Chlorella* and *Dunaliella salina*. The inactivation efficiency for *Chlorella* and *Dunaliella salina* reached nearly 98%.

The process could be conducted at a neutral pH of 8.3 (raw water) and 6.2, which break the restraint of strong acidic conditions. The pH has no obvious effect on the inactivation of algae and the removal efficiency of algal pollution.

Synergistic coupled effects of the oxidation of ·OH, coagulation and adsorption of iron hydroxide complexes, and oxidation of free chlorine, etc. in the Fe-ACF electro Fenton-like process were achieved at neutral pH conditions.

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