

# Electrochemical oxidation of quinoline aqueous solution on $\beta$ -PbO<sub>2</sub> anode and the evolution of phytotoxicity on duckweed

Xiangjuan Ma, Lixia Bian, Jingfeng Ding, Yaping Wu, Huilong Xia and Jionghui Li

## ABSTRACT

Electrochemical oxidation of quinoline on a  $\beta$ -PbO<sub>2</sub> electrode modified with fluoride resin and the comprehensive toxicity of intermediates formed during oxidation on duckweed were investigated in detail. The results showed that quinoline was initially hydroxylated at the C-2 and C-8 positions by hydroxyl radicals ( $\cdot$ OH) electro-generated on a  $\beta$ -PbO<sub>2</sub> anode, yielding 2(1H)-quinolinone and 8-hydroxyquinoline, then undergoing ring cleavage to form pyridine, nicotinic acid, pyridine-2-carboxaldehyde and acetophenone, which were ultimately converted to biodegradable organic acids. NO<sub>3</sub><sup>-</sup> was the final form of quinoline-N. The growth of duckweed exposed to the oxidized quinoline solution was gradually inhibited with the decrease in pH and the formation of intermediates. However, the growth inhibition of duckweed could be eliminated beyond 120 min of oxidation, indicating the comprehensive toxicity of the quinoline solution reduced when the amount of quinoline removed was above 80%. Additionally, the adjustment of the pH to 7.5 and the addition of nutrients to the treated quinoline solution before culturing duckweed could obviously alleviate the inhibition on duckweed. Thus, partial electrochemical degradation of quinoline offers a cost-effective and clean alternative for pretreatment of wastewater containing nitrogen-heterocyclic compounds before biological treatment. The duckweed test presents a simple method for assessing the comprehensive toxicity of intermediates.

**Key words** | duckweed, electrochemical oxidation, mechanism, phytotoxicity, quinoline

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## INTRODUCTION

Nitrogen-heterocyclic compounds (NHC<sub>s</sub>) like pyridine and its derivatives, indole, quinoline, etc. have received increasing attention due to their toxic, carcinogenic, mutagenic, and severe odour potential (Padoley *et al.* 2008), and their hazardous effects on ecosystem and human health (Stapleton *et al.* 2010). Pyridines have been rated as priority pollutants by the United States Environmental Protection Agency (Mathur *et al.* 2008) and extensively used for the production of pesticides, herbicides, pharmaceuticals, industrial solvents, dyes, rubber chemicals and so on (Acheson 1960), thereby frequently existing in the effluent of the aforementioned industries. Once NHC<sub>s</sub> enter into the environment, they can persist for long periods (Rogers *et al.* 1985), get easily transported through the soil and then contaminate ground water (Kuhn & Sufliata 1989) due to the fact that

their heterocyclic structure makes them more soluble than their homocyclic analogues (Padoley *et al.* 2008). In addition, the mutagenic potential of NHC<sub>s</sub> increases with the increasing number of rings: for example, quinoline is confirmed to be more mutagenic than pyridine (Mohammad *et al.* 1983). As a cost-effective process, biological oxidation using specific degradation bacteria is definitely becoming the primary choice to treat industrial wastewater containing quinoline. Various quinoline-degrading bacteria have been obtained, such as *Pseudomonas* sp. (Griese *et al.* 2006; Sun *et al.* 2009; Qiao & Wang 2010), *Burkholderia* sp. (Wang *et al.* 2001), *Rhodococcus* sp. (Zhu *et al.* 2008), *Comamonas* sp. (Cui *et al.* 2004), *Bacillus* sp. (Tuo *et al.* 2012), *Brevundimonas* sp. (Wang *et al.* 2015b) and so on. However, conventional biological processes are still restricted in

practical application because of some inherent shortcomings, such as the time-consuming acclimation of special microorganisms and high selectivity (Xing *et al.* 2012), long hydraulic retention time and poor quinoline concentration tolerance (Padoley *et al.* 2008). Advanced oxidation processes (AOP<sub>s</sub>) need to be eventually employed, which are capable of either the complete removal of the pollutant from wastewater or at the very least the destruction of the inhibition on biological activity due to the hydroxyl radicals ( $\cdot\text{OH}$ ) reaction (Yu *et al.* 2013). 91.5% of quinoline could be removed through photo-catalytic oxidation using  $\text{TiO}_2$  nanoparticles as a catalyst within 240 min under its optimized conditions (Jing *et al.* 2012). However,  $\text{TiO}_2$  is difficult to recover or separate from treated effluent, and may bring secondary environmental contamination (Ma *et al.* 2012). Electrochemical oxidation could overcome the aforementioned issues and is easy to regulate under a wide range of conditions by adjusting the current.  $\cdot\text{OH}$  electro-generated on the surface of a  $\beta\text{-PbO}_2$  anode (Cong *et al.* 2008) could effectively convert an aromatic pollutant to non-toxic and biodegradable organic acids (Wu *et al.* 2005). Nevertheless, it is worthwhile stressing that some intermediates formed during AOP<sub>s</sub> were more toxic than the parent pollutant. For instance, benzoquinone is the most toxic intermediate during electrochemical oxidation of phenol (Wu & Zhou 2001). 3,4-Dichloroaniline (3,4-DCA), one of the intermediates formed during electro-Fenton of diuron, was found to present a specific toxicity 90 times higher than diuron (Oturán *et al.* 2008). Therefore, not only the removal of parent compound but also the toxicity of degradation intermediates should be equally considered. However, separation and identification of all intermediates using chemical analysis are usually insufficient because of the enormous number of intermediates, which may be at a concentration too low to allow analytical determination. Consequently, it is difficult to predict the toxic property of the effluent using a physico-chemical approach. Hence, utilizing a biological test system with living cells or organisms may be the promising option, which can give a complete response to the complex mixture of intermediates without any prior knowledge of its composition or chemical properties (Radić *et al.* 2011).

Currently, the bioluminescence Microtox<sup>®</sup> standard method (Oturán *et al.* 2008; Dirany *et al.* 2010; Mousset *et al.* 2014), green alga (Oturán *et al.* 2008), specific oxygen uptake rate (Wang *et al.* 2015a) and duckweed test (Abdul *et al.* 2012) have been used to assess the comprehensive toxicity of treated effluent during AOP<sub>s</sub>. Among them, duckweed possesses physiological properties (small size, high multiplication rate and vegetative propagation) and may selectively accumulate

certain chemicals, thus it could serve as an ideal biological monitor to assess the toxicity of surface waters and wastewaters (Radić *et al.* 2011) that is more economical, intuitive and convenient. It is not necessary to conduct the test procedure axenically, and it is feasible to keep contamination by other organisms to a minimum. When electrochemical oxidation is employed to degrade the refractory pollutant, the electro-generated  $\cdot\text{OH}$  has the ability to disinfect the aqueous solution, implying that duckweed could be exposed directly to the effluent after oxidation.

In this study, electrochemical oxidation of quinoline using a  $\beta\text{-PbO}_2$  electrode modified with fluoride resin (Wu & Zhou 2001; Zhou *et al.* 2005) as anode was firstly carried out, and the effects of current density, initial pH and  $\text{Na}_2\text{SO}_4$  dosage on the removal of quinoline were investigated. High performance liquid chromatography (HPLC), ion chromatography (IC) and gas chromatography-mass spectrometry (GC-MS) analysis were applied to determine the formation of intermediates, based on which the electrochemical oxidation mechanism of quinoline on the  $\beta\text{-PbO}_2$  anode was postulated. Then the evolution of the toxicity of the quinoline solution with electrochemical oxidation time was determined through the exposure of duckweed to the oxidized solution over a period of 3–7 d. Chlorophyll a content ( $C_a$ ) and the frond number (FN) of duckweed measured with and without pH adjustment and the addition of nutrients to the oxidized quinoline solution prior to culturing the duckweed were chosen as the growth parameters.

## MATERIALS AND METHODS

### Reagents and chemicals

Quinoline was purchased from Sigma-Aldrich. Then 150 mg/L of quinoline aqueous solution was prepared by diluting quinoline in double distilled water, and the initial pH was 6.2. Methanol for HPLC analysis was chromatographic grade. Other chemicals used were analytical grade and purchased from Hangzhou Huipu Chemical Reagent Co. Ltd (Hangzhou, China).

### Electrochemical oxidation of quinoline aqueous solution

Electrochemical oxidation of quinoline was performed in an open, cylindrical, one-compartment and double layer Pyrex reactor (inner layer size:  $\Phi$  8.0 × 9.0 cm). Cooling water was passed through the hollow layer of the reactor to keep the solution at room temperature. For each set of experiments,

200 mL of quinoline solution was added into the reactor. The pH was adjusted to the desired value using 0.1 mol/L of H<sub>2</sub>SO<sub>4</sub> and 0.1 mol/L of NaOH solutions and measured with a pH meter (pH3110 SET2, Germany). A modified  $\beta$ -PbO<sub>2</sub> anode ( $\Phi$  4.5  $\times$  6.4 cm, effective area 90 cm<sup>2</sup>) was centered in the electrochemical reactor and surrounded by a stainless steel net cathode that covered the inner wall of the reactor. Constant current was maintained at the desired level with a digital DC power supply (WYL3010, Hangzhou, China). Samples were periodically taken for HPLC, GC-MS and IC analysis to examine the variation of quinoline concentration, the formation of main organic components and the transformation of quinoline-N. The removal of quinoline was calculated according to the concentration of quinoline before and after oxidation.

To ensure an adequate solution to cultivate the duckweed for the toxicity test, electrochemical oxidation of quinoline was performed in a bigger reactor (inner layer size:  $\Phi$ 10  $\times$  20 cm) using a  $\beta$ -PbO<sub>2</sub> anode ( $\Phi$  4.5  $\times$  20 cm, effective area 200 cm<sup>2</sup>) under 30 mA/cm<sup>2</sup> of current density, 2.0 g/L of Na<sub>2</sub>SO<sub>4</sub> and pH 6.2. 900 mL of quinoline solution was added into the reactor. Samples were taken after variable periods of oxidation time (up to 4 h) for the duckweed growth test to identify the phytotoxicity of the quinoline solution during electrochemical oxidation. The concentration of quinoline was also examined by HPLC. Chemical oxygen demand (COD) was determined in accordance with method 508C (closed reflux, colorimetric method) in *Standard Methods* (APHA 1998).

### Duckweed growth test

Duckweed was originally collected from a small pond at Xiaoshan City (China), which was free of obvious pollution sources, and maintained in nutrient solution for three months prior to toxicity testing. Nutrient solution for duckweed culture was prepared according to the OECD protocol (OECD 2006) and was adjusted to pH 7.5  $\pm$  0.1. The duckweed was pre-cultivated in nutrient solution for one week under continuous cool fluorescent light at an intensity of 8,000 lux and at 24  $\pm$  2 °C. Following the adaptation period, 20 healthy colonies with 2 fronds per colony were transferred to each 100 mL beaker containing 50 mL of oxidized quinoline solution. Duckweed grown on 2.0 g/L of Na<sub>2</sub>SO<sub>4</sub> solution served as a control. Then the beakers were covered with cling film that had 20 needle holes punched through the film to reduce evaporation and ensure that air could circulate. Finally, the beakers were placed into a biochemical incubator (GZX-300BSH-III, Shanghai, China) and taken out to be shaken by hand once every day. The temperature

and intensity of light in the biochemical incubator were controlled at 24  $\pm$  2 °C and 8,000 lux, respectively. Three replicates were prepared from each treatment. The FN in each beaker was recorded from 0 d to 7 d.

Samples of quinoline solution taken after several different reaction times were directly used to culture duckweed as soon as possible, this is because duckweed can grow easily in a wide range of pH values (3.5–10.5) (Khellaf & Zerdaoui 2010). C<sub>a</sub> and FN were used to evaluate the growth of duckweed. Additionally, in order to reduce the effect of pH variation on the growth of duckweed, the pH of the treated quinoline samples at different oxidation times, including the control, was adjusted to 7.5 and then the duckweed was cultured again. Similarly, in order to consider the effect of additional nutrients, the distilled water was replaced with partially-degraded quinoline solution for dissolving the nutrient salts to prepare the nutrient samples that were used to culture duckweed.

### Analytical methods

#### Determination of quinoline and intermediates

The concentration of quinoline was analyzed using an HPLC equipped with a UV detector (Agilent 1200, USA) and the wavelength was set at 254 nm for quinoline and 210 nm for carboxylic acids (Bielicka-Daszkiwicz *et al.* 2012). The samples were analyzed using a TC-C18 column (Agilent, 4.6 mm  $\times$  250 mm  $\times$  5  $\mu$ m). The mobile phase consisted of methanol:water (60:40, v/v) with a flow rate of 1.0 mL/min. Water buffered with phosphoric acid to pH 2.5 at a flow rate of 0.6 mL/min was used as the mobile phase during the separation of carboxylic acids. The column temperature was 30 °C and the injection volume was 20  $\mu$ L.

The main organic intermediates formed during quinoline degradation were analyzed by GC-MS (Agilent 7890A - 5973C, USA) with an HP-5MS column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). The samples were extracted by dichloromethane twice at a total volume ratio of 1 and nearly dried by a rotary evaporator (RE3000, China) at 40 °C, then filtered over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and subsequently concentrated to 1.0 mL by pressure blowing concentrator (MTN-28000, China) with high pure nitrogen. The injection volume was 2  $\mu$ L. The column temperature program for GC-MS was 40 °C isothermal for 2 min, and ramped to 300 °C with an increment of 7 °C/min, then holding for 15 min. MS analysis was performed at MS ion source of 230 °C and electron energy of 70 eV (Tuo *et al.* 2012). High pure helium was used as the carrier gas (1.0 mL/min). The injector temperature was 250 °C.

Evolution of inorganic ions during quinoline degradation was determined by IC (Dionex, ICS-90) equipped with a DS5 conductivity detector and an IonPac AS14 (250 mm × 4 mm (id)) anion-exchange column, linked to an IonPac AG14 (50 mm × 4 mm (id)) column guard. The mobile phase was a mixture of 3.5 mmol/L Na<sub>2</sub>CO<sub>3</sub> and 1.0 mmol/L NaHCO<sub>3</sub> with a flow rate of 1.2 mL/min. The injection volume was 10 μL. All samples were filtered through a 0.22 μm membrane before IC analysis.

### Evaluation of duckweed growth

The live FN (green part/total part ≥60%) was counted and recorded every day during the exposure period (7 d) and the protruding, distinctly visible fronds counted.

The C<sub>a</sub> of duckweed was determined by a spectrophotometric method (OECD 2006). After a particular time exposure for the toxicity test, all fronds in each beaker were put into a mortar containing 0.5 mL of acetone (90%, v/v) and crushed with a pestle. The homogenate was transferred into a 10 mL brown volumetric flask and rinsed to the mark line. The homogenate was mixed completely in the volumetric flask and then transferred to a 15 mL screw-cap centrifuge tube without rinsing the volumetric flask. After refrigerating for 2 h at 4 °C to extract chlorophyll a, the homogenate was mixed again and centrifuged at 2,000 r/min for 20 min. The optical density values of the supernatant at 663 nm and 645 nm were measured using a 1 cm quartz cuvette by a spectrophotometer (TU 1901, China) compared with 90% acetone solution. All the processes of chlorophyll extraction and determination were conducted in subdued light to avoid degradation. The amount of C<sub>a</sub> in each test container was indicated by the concentration of C<sub>a</sub> in the supernatant (Zhang & Jin 1997), which was calculated by inserting the corrected optical densities in the following equation:

$$C_a(\text{mg/L}) = 12.7OD_{663} - 2.69OD_{645} \quad (1)$$

## RESULTS AND DISCUSSION

### Electrochemical oxidation of quinoline

#### Effect of current density

Figure 1 illustrates the removal of quinoline as the function of reaction time under different current densities at pH 6.2,

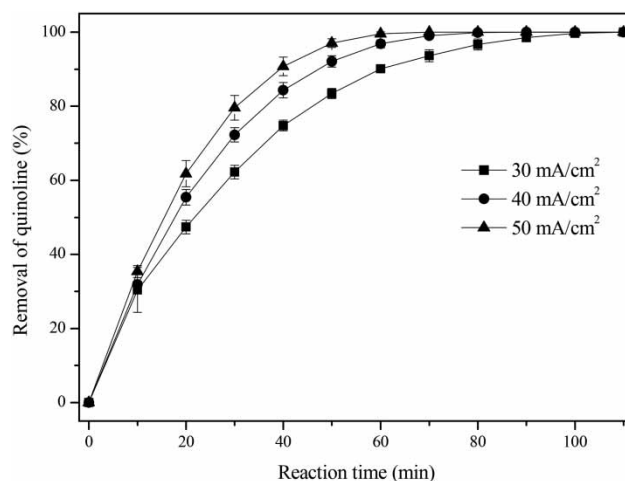


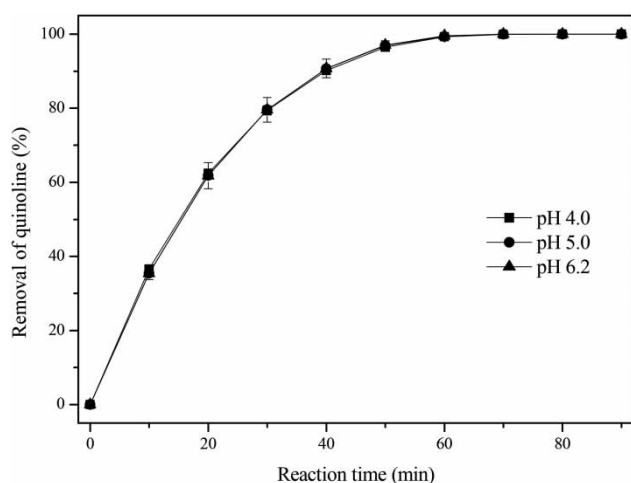
Figure 1 | Effect of current density on the removal of quinoline. Conditions: quinoline 150 mg/L, initial pH 6.2, Na<sub>2</sub>SO<sub>4</sub> 2.0 g/L.

150 mg/L of quinoline and 2.0 g/L of Na<sub>2</sub>SO<sub>4</sub>. Obviously, quinoline could be efficiently eliminated under the attack of ·OH generated on the surface of the β-PbO<sub>2</sub> anode, especially under higher current density. For instance, 98% of quinoline removal could be achieved within 80, 60 and 50 min of reaction under 30, 40 and 50 mA/cm<sup>2</sup> of current density, respectively. This is related to the fact that higher current density promotes the generation of ·OH radicals (Panizza & Cerisola 2009), thus enhancing the removal of quinoline.

#### Effect of initial pH

Many literatures have reported the influence of solution pH during anodic oxidation of organics on a PbO<sub>2</sub> anode, but the results are diverse and even contrary (Samet et al. 2006; Panizza et al. 2008), hence the effect of pH on the degradation performance of quinoline needs to be investigated. Considering that the β-PbO<sub>2</sub> anode is more favorable in acidic medium, the experiments were carried out within the pH range of 4.0–6.2 at 150 mg/L of quinoline, 2.0 g/L of Na<sub>2</sub>SO<sub>4</sub> and 50 mA/cm<sup>2</sup> of current density.

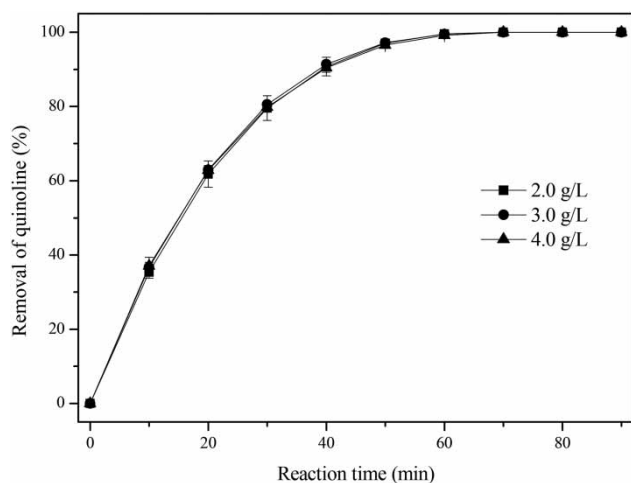
Figure 2 shows the effect of initial pH on the removal of quinoline at the surface of the β-PbO<sub>2</sub> anode. It can be observed that the degradation of quinoline was not dependent on the initial pH of the solution. This phenomenon could be explained by the pH value of the solution decreasing rapidly from 6.2 to 4.2 within the first 20 min of reaction, and then maintaining between 3.5 and 4.2 in the subsequent reaction time, which is the appropriate pH range for the activity of the β-PbO<sub>2</sub> anode. Therefore, pH 6.2 was chosen for further studies, which was the natural pH value of quinoline in water.



**Figure 2** | Effect of initial pH on the removal of quinoline. Conditions: current density 50 mA/cm<sup>2</sup>, quinoline 150 mg/L, Na<sub>2</sub>SO<sub>4</sub> 2.0 g/L.

### Effect of Na<sub>2</sub>SO<sub>4</sub> dosage

Figure 3 illustrates the effect of Na<sub>2</sub>SO<sub>4</sub> dosage on the removal of quinoline at pH 6.2 and 50 mA/cm<sup>2</sup> of current density. It was found that the removal of quinoline did not consistently correlate with the dosage of Na<sub>2</sub>SO<sub>4</sub>. However, the conductivity of the quinoline solution will significantly increase with the increase in Na<sub>2</sub>SO<sub>4</sub> dosage, resulting in a reduction of the energy consumption. Additionally, Na<sub>2</sub>SO<sub>4</sub> was not toxic to duckweed at a concentration up to 3.6 mmol/L (Abdul *et al.* 2012). Considering that an excess dosage of Na<sub>2</sub>SO<sub>4</sub> will affect the culture of duckweed in quinoline solution, 2.0 g/L of Na<sub>2</sub>SO<sub>4</sub> was sufficient for the following experiments.

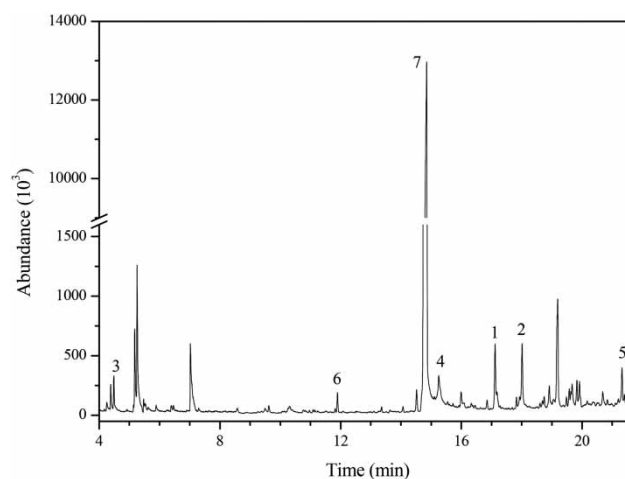


**Figure 3** | Effect of Na<sub>2</sub>SO<sub>4</sub> dosage on the removal of quinoline. Conditions: current density 50 mA/cm<sup>2</sup>, quinoline 150 mg/L, initial pH 6.2.

### Mechanism of electrochemical oxidation of quinoline

In order to investigate the main intermediates formed during electrochemical oxidation of quinoline at pH 6.2, 150 mg/L of quinoline, 2.0 g/L of Na<sub>2</sub>SO<sub>4</sub> and 50 mA/cm<sup>2</sup> of current density, the reaction mixtures were extracted by liquid-liquid extraction using dichloromethane as the extractant and then characterized by GC-MS analysis. Figure 4 demonstrates the gas chromatogram of treated quinoline solution after 60 min of electrochemical oxidation on a β-PbO<sub>2</sub> anode in a small reactor. The main organic components identified by GC-MS are listed in Table 1. The HPLC and IC analysis results showed that quinoline-N was finally converted into NO<sub>3</sub><sup>-</sup> after the cleavage of the pyridine ring under the successive attack of electro-generated ·OH. Simultaneously, oxalic acid, formic acid, acetic acid, propionic acid and fumaric acid were the main organic acids.

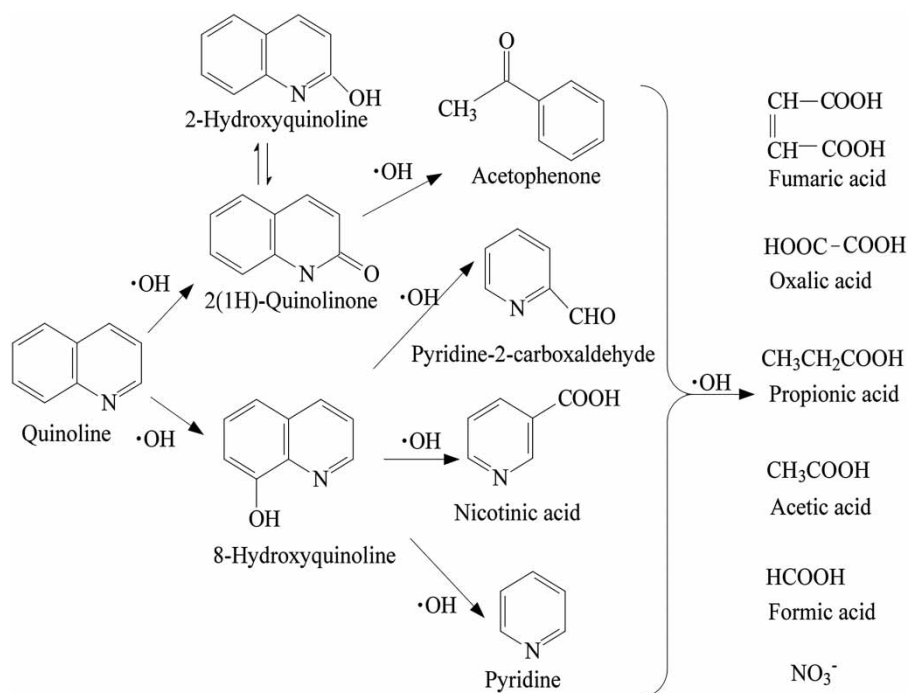
Based on the above results, the postulated electrochemical oxidation pathway of quinoline at the surface of the β-PbO<sub>2</sub> anode is presented in Figure 5. In the structure of quinoline, the N-atom of the pyridine ring has a strong electronegativity, which makes the density of the electron cloud in the pyridine ring less than the benzene ring. Generally, the electrophilic substituent reacts in the benzene ring and the nucleophilic substituent reacts in the pyridine ring (Tuo *et al.* 2012). The density of the π charge of C-2 is 0.8962, the lowest of all the atoms in the quinoline structure. Thus, the hydroxylation reaction may firstly occur at the C-2 position to yield 2(1H)-quinolinone and 2-hydroxyquinoline under the attack of ·OH. Simultaneously, the hydroxylation reaction also occurred at the C-8 position to yield



**Figure 4** | Gas chromatogram of quinoline solution after 60 min of oxidation on β-PbO<sub>2</sub> anode.

**Table 1** | Main organic components identified by GC-MS

Peak	Time (min)	Compounds	Chemical formula	Structure	CAS No.
1	17.18	8-Hydroxyquinoline	C <sub>9</sub> H <sub>7</sub> NO		148-24-3
2	18.01	2(1H)-Quinolinone	C <sub>9</sub> H <sub>7</sub> NO		59-31-4
3	4.17	Pyridine	C <sub>5</sub> H <sub>5</sub> N		110-86-1
4	15.25	Nicotinic acid	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>		59-67-6
5	21.32	Pyridine-2-carboxaldehyde	C <sub>6</sub> H <sub>5</sub> NO		1121-60-4
6	11.90	Acetophenone	C <sub>8</sub> H <sub>8</sub> O		98-86-2
7	14.85	Quinoline	C <sub>9</sub> H <sub>7</sub> N		91-22-5

**Figure 5** | Postulated electrochemical oxidation pathway of quinoline at the surface of  $\beta$ -PbO<sub>2</sub> anode.

8-hydroxyquinoline. Under the successive attack of  $\cdot\text{OH}$ , quinoline was subsequently cleaved, resulting in the formation of pyridine, nicotinic acid, pyridine-2-carboxaldehyde and acetophenone, which, containing one ring, could be further cleaved and transformed into

nontoxic, biodegradable and short-chain carboxylic acids (such as oxalic acid, formic acid, acetic acid, propionic acid and fumaric acid). This could be confirmed via the rapid pH drop of the quinoline solution due to the progressive accumulation of organic acids. When the reaction time

was 60 min, the pH of the solution reached the minimum value (pH 3.5), implying the slow degradation rate of organic acids during electrochemical oxidation. However, these organic acids could be easily utilized by organisms through conventional biological treatment.

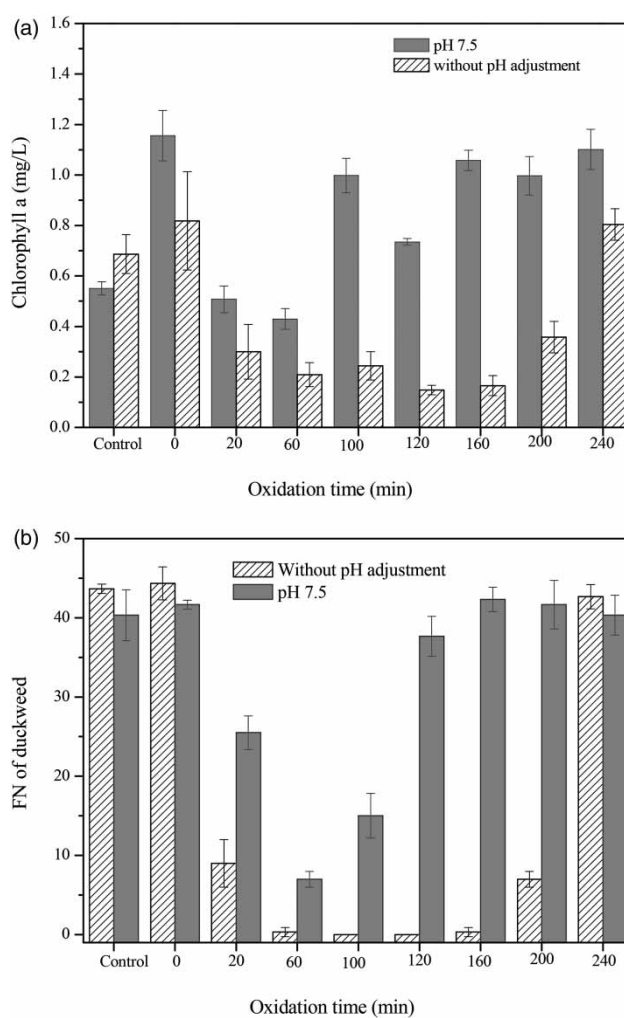
### Phytotoxicity assessment

The aforementioned results demonstrate that quinoline could be effectively removed by electro-generated  $\cdot\text{OH}$ , and some intermediates at low overall yields were formed during oxidation. It is crucial to assess the comprehensive toxicity of the effluent at different reaction times. In this part of the study, duckweed was directly or indirectly cultured in the effluent after electrochemical oxidation of quinoline under the following conditions: 30 mA/cm<sup>2</sup> of current density, 2.0 g/L of Na<sub>2</sub>SO<sub>4</sub>, and 150 mg/L of quinoline solution with an initial pH of 6.2. The phytotoxicity potential of the treated solutions was assessed according to the growth inhibition of duckweed.

### Effect of pH on growth parameters

Figure 6 shows the comparison of  $C_a$  content and FN of duckweed cultured in electrochemically-treated quinoline solutions directly and after pH adjustment to 7.5; the total culture time was 3 d. It can be seen that the  $C_a$  content of duckweed exposed to the solution after pH adjustment was all obviously higher than that of duckweed cultured directly.

When the duckweed was directly exposed to the effluent after 0 min and 60 min of oxidation time, the  $C_a$  of the duckweed decreased from 0.82 mg/L to 0.21 mg/L, indicating that the toxicity of the quinoline solution increased with the increase in oxidation time. When the pH of the treated solution was adjusted to 7.5, the  $C_a$  content of the duckweed correspondingly decreased from 1.16 mg/L to 0.43 mg/L. These observations indicate that the toxicity evolution of the effluent during the first 60 min of electrochemical oxidation is related not only to the variation in pH value but also to the toxicity of the intermediates formed. When the oxidation time was 60 min, the pH of the solution decreased sharply from 6.2 to 4.3, which significantly inhibited the growth of the duckweed. On the other hand, the formation of some cyclic intermediates might possess a strong inhibition to duckweed growth. Although 50% of the quinoline was removed at this time, the COD removal was only 36.8%, implying that the quinoline was not mineralized. Consequently, with the pH adjustment to 7.5, the growth inhibition of duckweed was not obviously alleviated,



**Figure 6** |  $C_a$  content (a) and FN (b) of duckweed exposed to different oxidized quinoline solutions 3 d directly and after pH adjustment to 7.5.

indicating that the toxicity of the effluent at the first 60 min might mainly come from some intermediates that may be more toxic to duckweed than quinoline. It was reported that the addition of one hydroxyl group at the C-8 position on quinoline caused a 40-fold increase in the inhibitory effect on the growth of *Toxoplasma* (Kadri et al. 2014) and 8-hydroxyquinoline had significant acute toxicity in adult *Cyprinus carpio* (Yan et al. 2015). With the prolonging of oxidation time to above 100 min, the intermediates were gradually converted to organic acids under the attack of  $\cdot\text{OH}$ , and the growth inhibition of duckweed was primarily caused by the decrease in the pH of the solution (from 4.3 to 3.8–4.0), and this could be elucidated from the reduction of the growth inhibition of duckweed. For example, the  $C_a$  contents of duckweed exposed to the solution after 160 min of oxidation with and without pH adjustment were 1.06 mg/L and 0.17 mg/L, respectively.

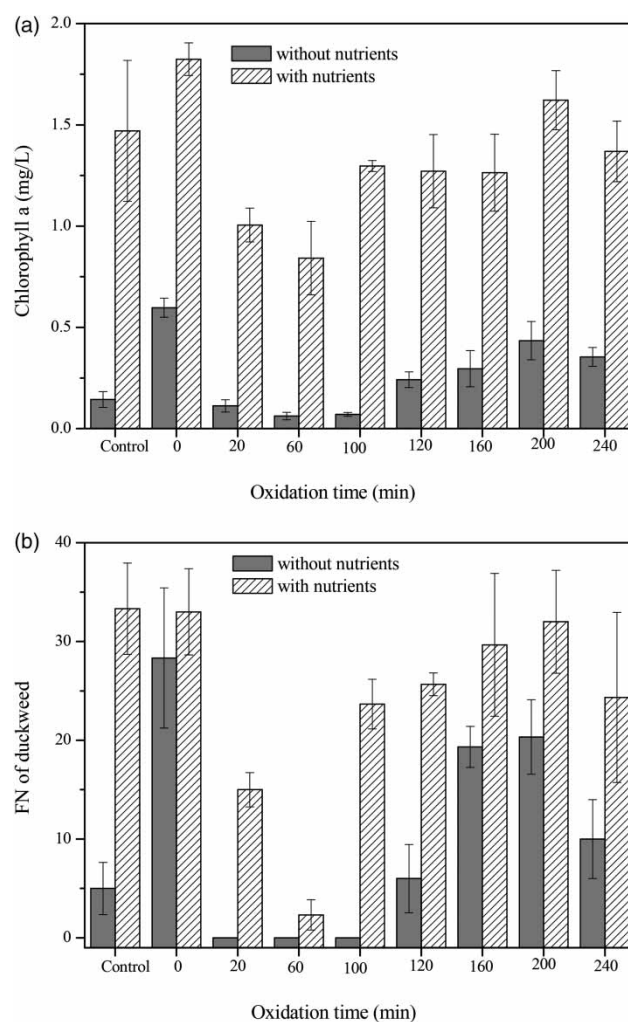
A similar trend of growth inhibition of duckweed was noticed with FN (Figure 6(b)). When the duckweed was exposed to the quinoline solutions after 60–160 min of oxidation, duckweed leaves started to look brown and gradually became black, and even died. However, once the pH was adjusted to 7.5, the FN significantly increased, especially when the duckweed was exposed to quinoline solutions after 120 and 160 min of oxidation, when the FN increased from 0 to 38 and 0.3 to 42, respectively. This also showed that the toxicity evolution of the quinoline solution after 100 min of treatment was mainly affected by the pH variation due to the formation of organic acids. Although pH adjustment could alleviate the growth inhibition of duckweed, the increasing amount of FN at 20 and 60 min was far less than that at 100–200 min. Therefore, the toxicity of the quinoline solution during electrochemical oxidation was mainly governed by the formation of toxic intermediates during the initial reaction period. The acidic medium played a dominant role in the phytotoxicity of duckweed due to the abundant accumulation of organic acids in the subsequent reaction period. On this account, ensuring a reaction time above 120 min and pH adjusted to 7.5, the toxicity of the effluent on duckweed could be disregarded.

### Effect of additional nutrients on growth parameters

Figure 7 demonstrates the effect of additional nutrients on the growth of duckweed exposed to quinoline solution treated at different oxidation times and pH adjusted to 7.5. The total exposure time was 7 days. It can be observed that about 1 mg/L of  $C_a$  content was increased for all samples due to the addition of nutrients. It was clearly observed that the 7 d FN of duckweed exposed to quinoline solution treated after 60 min of oxidation was almost zero, even when the additional nutrients were added. This phenomenon further confirmed the formation of some intermediates that contributed to the comprehensive toxicity of the quinoline solution. When the oxidation time was above 100 min, after the addition of nutrients and pH adjustment to 7.5, the inhibition of the treated quinoline solution on duckweed was not obvious. Hence, the appropriate oxidation time for quinoline solution before biological treatment was at least 120 min.

## CONCLUSIONS

Quinoline could be effectively removed through electrochemical oxidation using a  $\beta$ - $PbO_2$  anode doped with fluoride



**Figure 7** |  $C_a$  content (a) and FN (b) of duckweed exposed to different oxidized quinoline solution 7 d with or without additional nutrients.

resin, and was eventually converted to some biodegradable organic acids (such as oxalic acid, formic acid, acetic acid, propionic acid and fumaric acid); the quinoline-N was finally transformed to  $NO_3^-$ . The test of duckweed growth demonstrated that the formation of some intermediates indeed increased the comprehensive toxicity of the quinoline solution during electrochemical oxidation, especially after 60 min of oxidation. The inhibition of duckweed growth caused by the decrease in pH value due to the formation of organic acids could be alleviated through adjusting the pH of the treated quinoline solution to 7.5. Furthermore, the addition of nutrients to the treated quinoline solution was beneficial to the growth of the duckweed. Hence, quinoline solution under this study after 120 min of oxidation could be well used as a follow-up biological treatment.



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