Degradation of microcystin-RR using boron-doped diamond electrode

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ABSTRACT

Microcystins (MCs), produced by blue-green algae, are one of the most common naturally occurring toxins found in natural environment. The presence of MCs in drinking water sources poses a great threat to people's health. In this study, the degradation behavior of microcystin-RR on boron-doped diamond (BDD) electrode was investigated under galvanostatic conditions. Such parameters as reaction time, supporting electrolyte and applied current density were varied in order to determine their effects on this oxidation process. The experimental results revealed the suitability of electrochemical processes employing BDD electrode for removing MC-RR from the solution. However, the efficient removal of MC-RR only occurred in the presence of sodium chloride that acted as redox mediators and the reaction was mainly affected by the chloride concentration (c_{NaCl}) and applied current density (I_{appl}). Full and quick removal of 0.50 μg/ml MC-RR in solution was achieved when the operating conditions of c_{NaCl} and I_{appl} were 20 mM and 46.3 mA/cm^2, or 35 mM and 18.2 mA/cm^2 respectively. The kinetics for MC-RR degradation followed a pesudo-first order reaction in most cases, indicating the process was under mass transfer control. As a result of its excellent performance, the BDD technology could be considered as a promising alternative to promote the degradation of MC-RR than chlorination in drinking water supplies.

1. Introduction

The increase of population and the consequent intensification of agricultural and industrial activities have led to eutrophication in superficial freshwater bodies, which causing frequent cyanobacteria blooms worldwide. In China, the situation is grim especially in our living area near *Taihu* lake. Among the most common types of cyanotoxins found in natural waters are microcystins (MCs), a family of hepatotoxic cyclic peptides. Besides their potent toxicity towards plants and animals, the presence of sublethal doses of MCs in drinking water is implicated as one of the key risk factors for the usual high occurrence of primary liver cancer observed in China [1]. Over 76 different analogues of MCs, one of them is microcystin-RR (MC-RR, $C_{49}H_{75}N_{13}O_{12}$, MW 1038.2), has been isolated from natural blooms or laboratory cultures of cyanobacteria [1,2], and is far more common than other MCs in Asia due to the higher temperature [3] and it will make more sense to choose it for the present study.

MCs are known to be very chemically stable compounds because of their cyclic structure [4,5]. The toxicity of MCs coupled with their stability is of concern in water supply, so methods of removing these compounds and their behavior in the presence of various oxidants warrant investigation. Since conventional methods in drinking water treatment such as coagulation and sedimentation have only limited efficacy in removing MC-RR from potable waters, research efforts are then needed to develop some powerful alternatives. Recent studies show that photocatalysis, ultrasounding, chlorination, ozonation and permanganate are effective for the destruction of dissolved MCs [6–11]. It has been also shown that MCs can be eliminated from natural waters by membrane filtration, microbial approaches and gamma radiation, but all these options have drawbacks in certain aspects [12–14].

In recent years, electrochemical oxidation, as a popular procedure for water treatment, has drawn increasing research attentions because it is environmental friendly, amendable to automation and is capable of destructing a variety of biorefractory contaminants effectively [15]. Also, the recent advent of boron-doped diamond (BDD) electrode has hastened the development of this technology for real applications. BDD electrode is an excellent hydroxyl radical generator providing wide potential window, high overpotential for oxygen evolution, and unique electrocatalytic properties in the destruction of organic pollutants [15,16]. These properties make BDD electrode an ideal candidate for kinetic study in the field of environmental electrochemistry. Over the past decade, BDD electrode has been successful applied to the treatment or degradation of phenols, dyes, benzene and other toxic chemicals [17–20]. But

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to our knowledge, we found that few reports had appeared on the removal of natural toxins using electrochemical methods.

Therefore, the present paper aims at the exploitation of the feasibility of removing MC-RR by anodic oxidation on BDD electrode. In order to optimize the electrochemical oxidation of MC-RR, the main influencing factors such as reaction time, electrolyte concentration and applied current density on the degradation rates are mainly evaluated. Also, kinetic analysis is conducted and the energy consumption is calculated based on the removal rate of MC-RR.

2. Experimental

2.1. Materials

MC-RR (HPLC-grade) was purchased from ALEXIS Biochemicals (Switzerland), while trifluroacetic acid (TFA) and HPLC-grade methanol were from Tedia (USA) and Merck (Germany), respectively. NaCl, KCl, K_2SO_4, KNO_3, Na_2CO_3 and H_2SO_4, all provided by Shanghai Chemical Reagent Co. (Shanghai, China), were of analytical grade and used without further purification. All stock solutions were carefully prepared using deionized water obtained from AVP-2-35G-01 Water-system (Millipore, USA). Natural water from *Taihu* lake was fetched from Meiliangwan Bay (Wuxi, China). Hypersil ODS C_{18} cartridges were purchased from USA. ELISA reagents for MCs detection with the detection limit of 0.10×10^{-3} μg/ml were made by Beacon (USA).

Si/BDD (BDD, boron-doped diamond thin film) electrode, prepared by microwave plasma-assisted chemical vapor deposition, was supplied by Kanagawa Academy of Science of Technology (Japan), the same size stainless steel plate with high dimensional precision and fine-polished surface was provided by Nanjing Yanziji Manufacturing Factory (Nanjing, China). Both electrodes were square type plate with the effective surface area of 3.24 cm².

2.2. Analytical apparatus

The decay of MC-RR concentration was mainly measured by HPLC (Aligent 1100, Germany) equipped with G1314A UV Detector. The separation column was reversed-phase Krosmasil C_{18} column (4.6 mm × 250 mm, 18 μm) from AKZO NOBEL equipped with a DIKMA C_{18} guard cartridge (Dikma Tech., USA). The pH of the solution was monitored with PH S-25 pH meter, and the conductivity measurements were followed in DDB-303 conductivity meter with a DJS-1C electrode. Both meters were made in Shanghai LEICI Corporation (Shanghai, China). The concentrations of nitrate and chloride ions were determined using ion selective electrode (Shanghai, China).

2.3. SPE–HPLC analytical procedure of MC-RR

Samples with MCs concentrations over 0.2 μg/ml could be injected directly; otherwise the samples should be preconcentrated prior to analysis by solid phase extraction (SPE) due to their trace concentrations. Following the general procedures of SPE, the Hypersil ODS C_{18} cartridge was conditioned firstly by 10 ml methanol, followed by 10 ml deionized water, then 20 ml sample was passed through the cartridge under vacuum at a flow rate of 5 ml/min. Afterwards the cartridge was rinsed, in turn, with 10 ml portions of deionized water, 20 ml portions of 10% methanol and 20 ml portions of 20% methanol aqueous solution, MC-RR was eluted out from the cartridge using 5 ml 80% methanol containing 1.0% TFA under vacuum at a flow rate of 1.0 ml/min. Finally, the eluate was dried in nitrogen flow, and MC-RR was dissolved with 0.4 ml methanol before being analyzed by HPLC. Chromatographic conditions were as follows: the mobile phase was methanol/water containing 0.10% TFA (62:38, v/v); flow rate of 1.0 ml/min operat-

ing at wavelength of 238 nm for detection; an inject volume of 20 μl and a constant column temperature of 25 °C. Under the conditions, a typical HPLC curve of MC-RR samples displayed a well-defined peak for MC-RR at retention time of 7.0 min. The concentration of MC-RR was determined by developing a calibration curve, as reported in literature [8].

In addition, some characteristics of the natural water samples from *Taihu* lake were checked. To obtain the overall content of MCs, the water samples were first submitted to filtration using Millipore 0.45 μm film and then to detection with ELISA reagent. While to determine the concentration of MC-RR, 400 ml lake water being filtered should go through the SPE–HPLC process described above. Results showed that the contents of overall MCs and MC-RR in lake water samples were 4.34×10^{-3} μg/ml and 2.46×10^{-3} μg/ml, respectively.

2.4. Electrochemical experiments

Experiments were mainly performed in a laboratory scale reactor which consisted of a 50 ml cylindrical one-compartment glass cell, and a magnetic stirrer at a constant stirring rate of 350 rpm. The BDD plate served as anode in this standard parallel plate electrochemical cell, the same size stainless steel plate as cathode and with the electrode gap of 7 mm. Water samples containing 0.50 μg/ml MC-RR and desired concentrations of electrolyte salts were introduced into the cell and continuously stirred in order to keep homogeneous, its temperature being maintained at 20 °C by a cooling jacket. The processed volume was 20 ml in each run, which yielded a surface area to volume ratio (S/V) of 0.162/cm. The surface of BDD was cleaned by ethanol and ultra-pure water successively before each reaction, and the treated water samples were collected from the cell at various intervals for analysis. All experiments were carried out at least in duplicate and good reproducibility was obtained.

The concentrations of residual MC-RR ($c_{RR,t}$) in the reaction mixture were analyzed following the HPLC or SPE–HPLC method developed above. ELISA was employed only in a few cases when $c_{RR,t}$ was below the detection limit of SPE–HPLC (4.0×10^{-3} μg/ml). For simplicity, we used series code such as RR-01 and RR-02 to stand for the different experimental entries. Note that it was impossible to adjust the pH values of the abundant natural or tap water; all experiments were conducted at natural conditions without pH adjustment except for RR-01 as an example for discussion.

3. Results and discussion

3.1. Effect of reaction time

Fig. 1A shows the degradation rate of MC-RR as a function of electrolysis time operating at pH of 3.23 (adjusted with 1.0 M H_2SO_4). It can be observed that the removal rate increases linearly with time at the beginning, but after 30 min, extended reaction time has no notable effect on further degradation of MC-RR. The kinetic trend is reasonable because relatively high $c_{RR,0}$ will result in a high reaction rate, when it is gradually used up, the rate decreases rapidly. As can be seen, 86.8% MC-RR is removed at 30 min, 98.5% at 60 min, and full removal is achieved after 2 hours. As a result, RR-01 can be considered as a perfect reaction following pseudo-first order with the rate constant (k_1) of 0.070 min⁻¹ (R^2 = 0.9995). In Fig. 1B, Point **M** stands for the concentration of MC-RR (c_{RR}) which is close to that of lake water (2.46×10^{-3} μg/ml), and Point **N** refers the c_{RR} which can not be detected even by ELISA (<0.10×10^{-3} μg/ml), indicating the total destruction of MC-RR. The time duration between these two points is about 30 min, and similar behavior can be also found in several other entries.
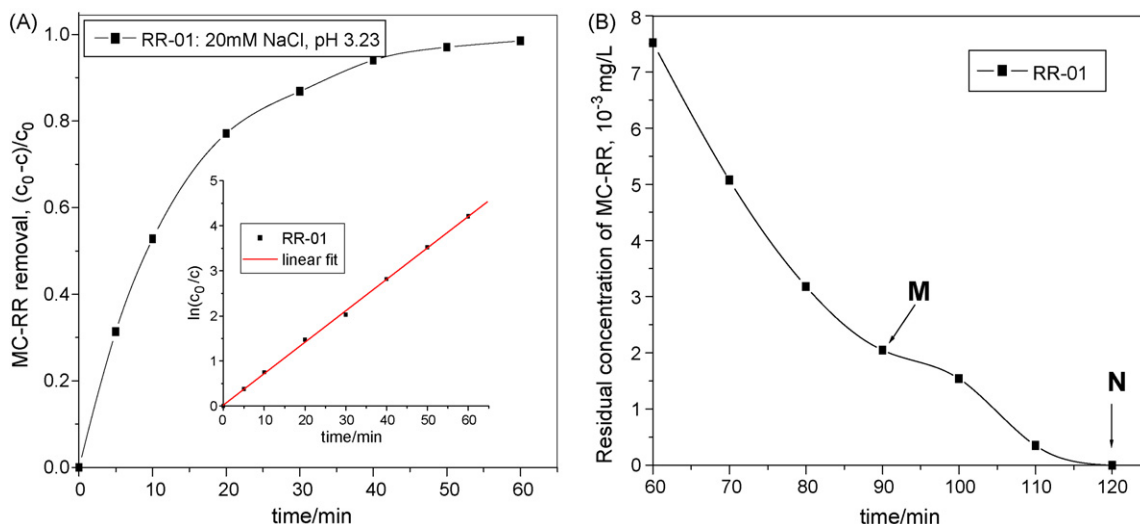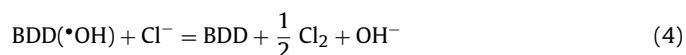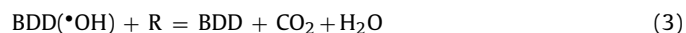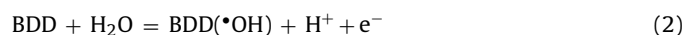
Fig. 1. (A) MC-RR removal rate as a function of time ($c_{RR,0}$: 0.5 μg/ml, current density (I_{appl}): 18.2 mA/cm^2, supporting electrolyte: 20 mM NaCl, pH 3.23), insert: the linear fit results of RR-01; (B) variation of residual MC-RR concentration during reaction time from 60 min to 120 min.

It is a common sense that Cl$^-$ is oxidized via direct electron transfer on most electrodes (reaction (1)). However, Cl$^-$ can also be oxidized by hydroxyl radicals ($^\bullet$OH) produced in an AOP (advanced oxidation processes) [21]. In the present entry, part of $^\bullet$OH generated on BDD anode may be consumed to produce active chlorine according to reactions (4) and (5) instead of being reacted directly with organic pollutants (R) as expressed in reaction (3): [15]

$$Cl^- - e^- = \frac{1}{2}Cl_2 \tag{1}$$

$$BDD + H_2O = BDD(^\bullet OH) + H^+ + e^- \tag{2}$$

$$BDD(^\bullet OH) + R = BDD + CO_2 + H_2O \tag{3}$$

$$BDD(^\bullet OH) + Cl^- = BDD + \frac{1}{2}Cl_2 + OH^- \tag{4}$$

$$Cl_2 + H_2O = Cl^- + HClO + H^+ \tag{5}$$

The good performance observed in RR-01 is indicative of the strong oxidizing power of Cl$_2$ and HClO [22]. Besides, by comparing RR-01 and RR-02 (see Fig. 2, at natural pH), we may also see the enhanced oxidizing activity of HClO at lower pH. Considering the removal efficacy and the manipulate costs, 60 min is determined as the reaction time for evaluating other parameters.
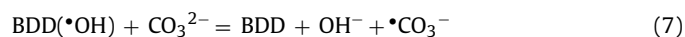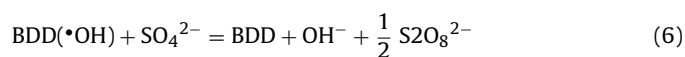
3.2. Effect of adding supporting electrolyte

To clarify the roles of different electrolytes in electrochemical degradation of MC-RR, a series of inorganic salts with the concentration of 20 mM were employed into the comparative study (RR-02 to RR-06).

The results clearly demonstrate the impacts of different electrolytes on the degradation of MC-RR (Fig. 2). First, let us focus on the clear difference shown between RR-02 and RR-03; it seems that the influence of cations during the electrolysis must be taken into consideration. Since the effect has not been reported before, we propose several factors lead to this distinction as (1) the different activities of KCl and NaCl in aqueous solutions; (2) different migration rates of cations (0.390 for 20 mM NaCl and 0.490 for 20 mM KCl); (3) some unknown interactions between salts and MC-RR ring, which consists of several amino acids. The phenomenon is rather interesting and calls for further investigation.

Next, in the presence of sulfate or carbonate, the degradation rate is comparatively poor and reactions kinetics appears to be complex (RR-04 and RR-05). This underperformance can be linked to

the formation of peroxides which decompose less efficiently in the absence of heat or UV light, resulting in lower removal rate of MC-RR for the invalid consumption of $^\bullet$OH [16] (reactions (6) and (7))

$$BDD(^\bullet OH) + SO_4^{2-} = BDD + OH^- + \frac{1}{2}S_2O_8^{2-} \tag{6}$$

$$BDD(^\bullet OH) + CO_3^{2-} = BDD + OH^- + {}^\bullet CO_3^- \tag{7}$$

Nitrate ions do not form peroxides as sulfate or carbonate ions do [15], so the majority of MC-RR degradation must be occurring in bulk solution by $^\bullet$OH pathways (RR-06), which is also in agreement with the fact that the concentration of nitrate ions remains unchanged during the electrolysis (not shown here).

Since NaCl is proved to be the best one among the salts chosen for study, the influence of its initial concentration towards the degradation of MC-RR is investigated over a range of 10–35 mM. As it can be apprehended from Fig. 3, the increase of NaCl concentration leads to a quick promotion on the removal rate of MC-RR.
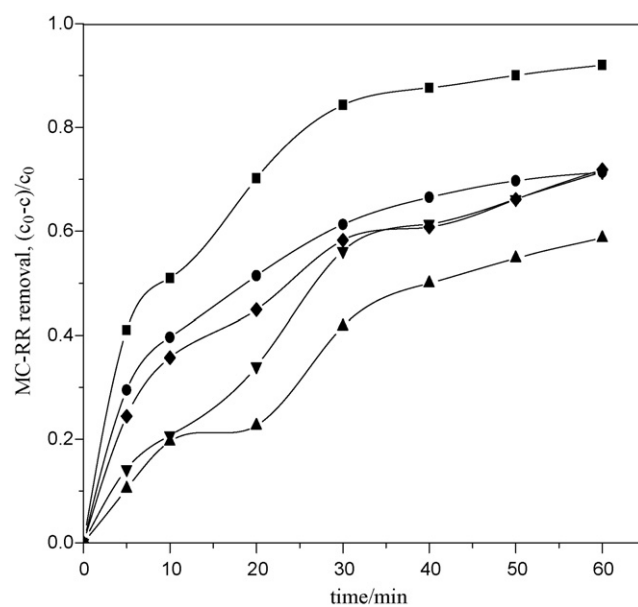

Fig. 2. MC-RR removal rate versus different supporting electrolyte (■, RR-02, 20 mM NaCl); (●, RR-03, 20 mM KCl); (▼, RR-04, 20 mM K$_2$SO$_4$); (▲, RR-05, 20 mM Na$_2$CO$_3$); (♦, RR-06, 20 mM KNO$_3$); $c_{RR,0}$: 0.5 μg/ml, I_{appl}: 18.2 mA/cm^2, no pH adjustments.
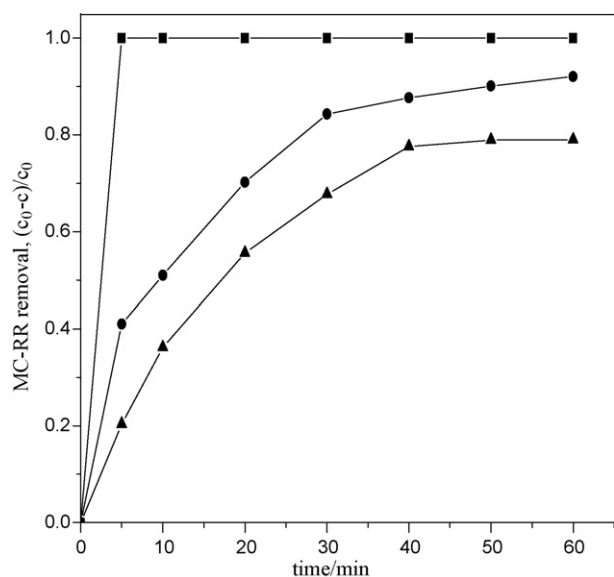
Fig. 3. MC-RR removal rate versus concentrations of sodium chloride (■, RR-07, 35 mM NaCl); (●, RR-02, 20 mM NaCl); (▲, RR-08, 10 mM NaCl); $c_{RR,0}$: 0.5 μg/ml, I_{appl}: 18.2 mA/cm².

As c_{NaCl} reaches 35 mM, the destruction is so rapid that MC-RR is undetectable by the first sampling point (5 min). This proves that the effect of NaCl concentration is very positive for the destruction of MC-RR molecules due to a rise in active chlorine generation. Previous reports [9] reveal that there exists an optimal dosage of Cl₂ for the complete removal of MCs by chlorination, our results also indicate a sudden rise or a jump in the oxidation capabilities in NaCl dosage from 20 to 35 mM, which may be considered as a factor for the full removal of MC-RR by electrochlorination with BDD electrode.

### 3.3. Improvement of performance by adjusting applied current density

It can be concluded that there is a clear trend towards an increase of the degradation efficacy with rising current densities, for the formation rate of active chlorine or other oxidation species are certainly higher at higher currents [22]. Besides, it is well known that

chlorine of high concentrations in water infection may form irritating carcinogenic byproducts, thus a higher applied current and a lower salt concentration are preferred in practice for such processes. In the following study, different current densities ranging from 9.1 to 46.3 mA/cm² are employed to study the effects involved, with 20 mM chosen as the optimal dosage of NaCl.

As represented in Fig. 4A, the quick and full destruction of MC-RR is obtained again as I_{appl} reaches 46.3 mA/cm², which can be attributed to the increase of mass transfer coefficient due to the increase of oxygen evolution [23]. In order obtain more information on this process, a comprehensive model concerning the degradation behavior of organics in BDD system [15], is employed. In it, an important constant named limiting current density (I_{lim}) is defined in Eq. (8):

$$I_{lim} = 4\mathbf{F} k_m COD \tag{8}$$

where $\mathbf{F}$ is Faraday's constant, k_m is the average mass transport coefficient (roughly 10^{-5} m/s). Although common measurements such as COD, TOC and CV are unfit in our system, we try to make a rough calculation so as to evaluate the orders of magnitude of limiting current and mass flux. The COD value is calculated by the following equation:

$$\underset{\substack{0.5mg/l}}{C_{49}H_{75}N_{13}O_{12}} + 61.75\,O_2 = 49CO_2 + 6.5N_2 + 37.5H_2O$$
$$\underset{\substack{COD}}{}$$
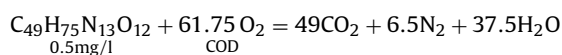
$$COD = \frac{0.50 \times 61.75}{1038.2} = 0.0297 (mol\,O_2/m^3) \tag{9}$$

$$I_{lim} = 4\mathbf{F} k_m\,COD = 4 \times 96484.5 \times 10^{-5} \times 0.0297$$
$$= 0.115\,A/m^2 = 0.012\,mA/cm^2$$

The result of $I_{appl} \gg I_{lim}$ clearly indicates that the electrolysis is under mass transfer control, and the reaction follows an exponential trend due to the mass transfer limitation [15]. According to Eq. (8), high current efficiency is favored with lower I_{appl}, higher $c_{RR,0}$ and higher k_m. But a high I_{appl} will promote the intensified generation of both H₂ and O₂ by splitting water; meanwhile a higher k_m is obtained due to the extra stirring effect of these bubbles in the solution. Next, by comparing the three entries (RR-02, RR-10 and RR-11), we may see that the distinctions are not marked whatever. The loss of efficiency with increasing current can be associated with
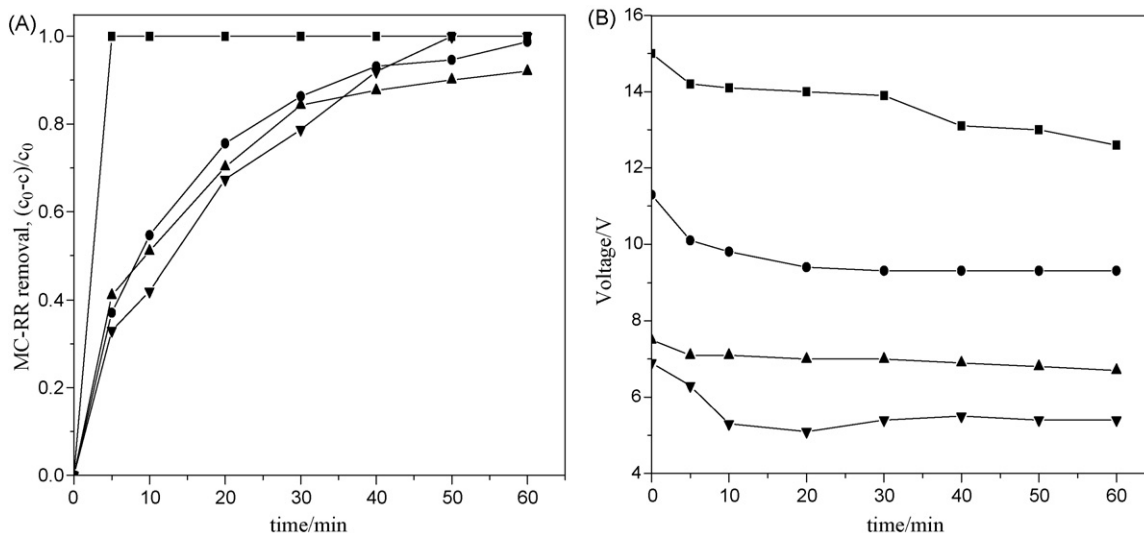

Fig. 4. (A) MC-RR removal rate versus applied current density; (B) variation of cell potential during electrolysis process. (■, RR-09, 46.3 mA/cm²); (●, RR-10, 27.8 mA/cm²); (▲, RR-02, 18.2 mA/cm²); (▼, RR-11, 9.1 mA/cm²); $c_{RR,0}$: 0.5 μg/ml, supporting electrolyte: 20 mM NaCl.

Table 1
The degradation kinetics of MC-RR on BDD anodes fitting pseudo-first order reaction.

Entry	Reaction equations	Rate constants (min^{-1})	Half life $t_{1/2}$ (min)	Correlation coefficient, R^2
RR-01	$\ln(c/c_0) = -(0.070 \pm 0.001)t$	0.070 ± 0.001	9.9 ± 0.1	0.9995
RR-02	$\ln(c/c_0) = -(0.065 \pm 0.004)t$	0.065 ± 0.004	10.7 ± 0.7	0.9894
RR-03	$\ln(c/c_0) = -(0.058 \pm 0.003)t$	0.058 ± 0.003	12.0 ± 0.5	0.9931
RR-04	$\ln(c/c_0) = -(0.047 \pm 0.005)t$	0.047 ± 0.005	14.7 ± 1.1	0.9639
RR-05	$\ln(c/c_0) = -(0.049 \pm 0.004)t$	0.049 ± 0.004	14.1 ± 1.0	0.9894
RR-06	$\ln(c/c_0) = -(0.046 \pm 0.004)t$	0.046 ± 0.004	15.1 ± 1.2	0.9826
RR-08	$\ln(c/c_0) = -(0.058 \pm 0.002)t$	0.058 ± 0.002	12.0 ± 0.4	0.9964
RR-10	$\ln(c/c_0) = -(0.063 \pm 0.002)t$	0.063 ± 0.002	11.0 ± 0.3	0.9989
RR-11	$\ln(c/c_0) = -(0.068 \pm 0.005)t$	0.068 ± 0.005	10.2 ± 0.7	0.9845

the smaller relative proportion of reactive BDD($\bullet$OH) generated, since this radical is wasted more rapidly via oxidation to oxygen gas [23].

Besides, in the range of I_{appl} employed in the present study, the anodic potential is found to be in the region of water decomposition ($V > 2.3$ V), thus no electrode fouling problem encounters [24]. The last observation that can be noticed is the variation of the conductivity of the wastewater under different applied currents (Fig. 4B). A decrease in the cell potential in the initial stage and later the stabilization of the potential to a constant value, may be defined as the characteristics feature for such electrochemical processes.

3.4. Reaction kinetics

The degradation behaviors of MC-RR on BDD electrode were subjected to the analysis of kinetic equation, good fitting were found for pseudo-first order reaction for most entries (Table 1). The results can be interpreted in terms of reaction limited by mass transfer as discussed above, which are also consistent with the fact that degradation process was a bi-molecular reaction between MC-RR and oxidant ($\bullet$OH or Cl_2) of a constant yield. It is found that MC-RR decay in several cases has deviations to certain extent in fitting pseudo-first order, possibly resulting from the competitive consumption of oxidants by parallel reactions with intermediates [25].

All experiments conducted above are aimed to study the degradation behavior of MC-RR on BDD electrode, and some results are similar to the work of Shi [22], in which the degradation kinetics of MC-RR on DSA electrode are investigated. However, it should be noted that, in the field of drinking water treatment, BDD electrode is still a much better choice than other electrodes for its non-toxicity, outstanding chemical stability and long service life (theoretically 40–50 years) [15].

As can be seen, the initial concentration of MC-RR ($c_{RR,0}$) employed in the present study greatly exceeds those of possibly lake or tap water. The kinetic trend proposed by Shi indicates that the c_{NaCl} and I_{appl} values needed both decrease correspondingly as $c_{RR,0}$ decreases [22]. In an additional experiment, using the same reactor, when $c_{RR,0}$ is decreased to 0.25 μg/ml or lower, the full destruction is achieved within 5 min under the operating conditions of RR-02 (20 mM for c_{NaCl} and 18.2 mA/cm^2 for I_{appl}, respectively). Considering chlorides ions are naturally present in superficial waters, it seems feasible to use the BDD technology directly for the detoxification of MCs in potable waters. With this in mind, we decide to perform a simulated experiment with the aim to explore the feasibility of this technology for practical applications. In it, the tap water from Wuxi city is employed. This tap water contains about 0.5 mM Cl$^-$, all together with other salts (including SO_4^{2-}, CO_3^{2-}, NO_3^-, in much lower concentrations) shows a conductivity of 245 μS/cm. Also, $c_{RR,0}$ used is confined to the scope of $(0.5-4.0) \times 10^{-3}$ μg/ml, which is the possible level of MCs concentration during cyanobacterial blooms. Excitingly, the application of a current density of 46.3 mA/cm^2 results in a quick degradation of the toxin. In other words, MC-RR is completely removed within 1 min in the presence

of these natural salts in tap water as electrolyte. Despite the high S/V ratio of the system used in the present study, this high reaction rate offers promising prospects for practical applications, which means that similar removal rate can be obtained at much lower S/V ratio by extending reaction time or by adjusting applied currents.

Last, the energy consumption is calculated for the treatment of 1 m^3 of MC-RR solution. For an electrochemical reactor working in galvanostatic conditions, the electrolysis energy is given by Eq. (10):

$$\mathbf{E} = \int_t U(t)I\,dt \tag{10}$$

where $\mathbf{E}$ is energy consumption, U is the voltage and I is the applied current.

For several selected entries following pseudo-first reaction, the energy consumption is shown in Fig. 5. The results demonstrate a progressive increase in energy consumption and a decrease in removal efficacy with increasing current densities. This tendency agrees with the average cell voltage required at greater currents and the behavior stated above for current efficiencies. Consequently, the application of lower applied current densities seems to be more advantageous for such processes than with large ones. However, smaller energy consumption is also obtained in cases such as RR-07 or RR-09. For example, the energy required for the treatment of 1 m^3 of solution in RR-02 is 25.10 kWh, but it only takes 1.75 kWh for RR-07 and 8.75 kWh for RR-09, respectively. This difference is directly linked to the electrolysis time required for the complete disappearance of MC-RR. In the view of the amount of MC-RR removed, the energy consumption is about 20 mg MC-RR/kWh for RR-02, which makes the process undesirable. Given the small size of the BDD elec-
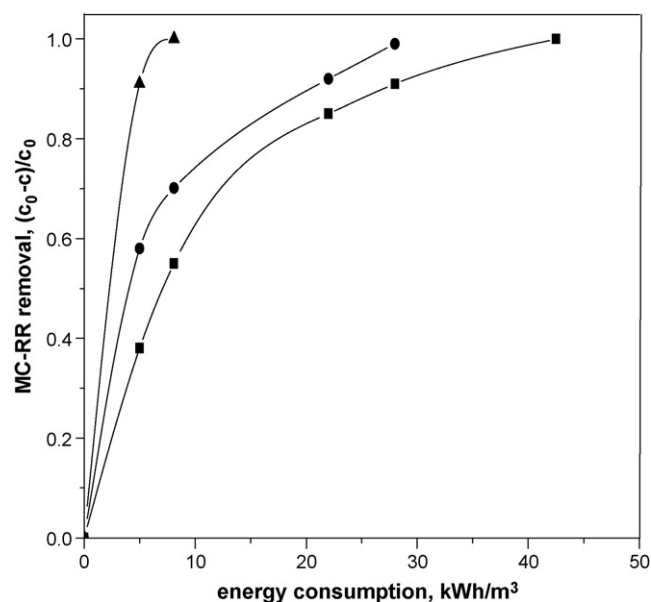

Fig. 5. MC-RR removal as function of energy consumption during anodic oxidation on BDD electrode. Selected entries: (■) RR-10; (●) RR-02; (▲) RR-11.
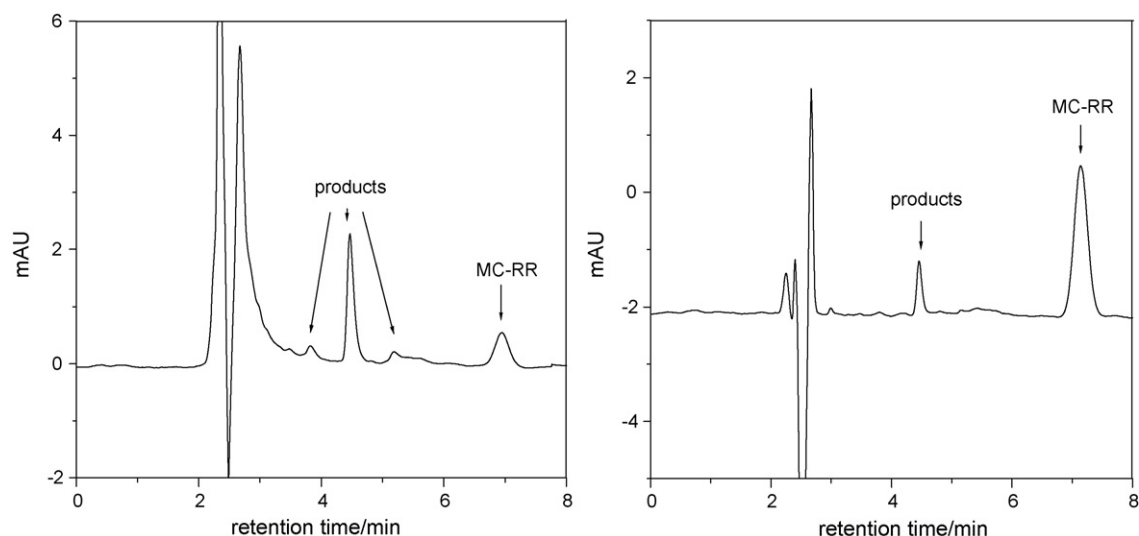
Fig. 6. Chromatogram obtained from HPLC analysis of two selected water samples.

trode employed (3.24 cm^2) and the long electrolysis time required, it is hard to obtain a great current efficiency and a low energy cost under the present operating conditions. Thus, this problem is expected to be solved by further optimizing the operating conditions, or by employing BDD electrode with large size, although it is not yet commercially available.

3.5. Discussions on byproducts formation

Fig. 6 shows two typical HPLC features of the water samples after being treated. A new peak (sometimes several) appears around 4.3 min with a considerable range of absorbance value compared with that of MC-RR, and the peak area is fluctuating continuously during electrolysis. Due to the continuous generation/consumption process of the degradation intermediates, the general rules of the variation are very hard to be determined. Furthermore, LC/MS fails to identify the degradation byproducts in several trials owing to their trace concentrations and complex compositions. In fact, given the big molecular weight and variety of functional groups presented in MC-RR, it is a daunting task to identify the individual byproducts and assess their individual biological activities. We choose to undertake a shrimp-feed experiment to test the toxicity of the BDD-treated solution (with MC-RR completely removed). In agreement with the correlative literature reports [26–30], no toxicity is detected.

Returning to RR-02, the diffusion flux of MC-RR and Cl$^-$ in this entry are 4.8×10^{-9} and 2×10^{-5} mol/(s m^2), respectively. Under such conditions, the main reactions may be the actions between MC-RR and Cl$_2$ in the bulk rather than the actions at the electrode surface. Previous excellent works [28–29] have suggested the main routes of MCs degradation being attacked either by •OH or Cl$_2$ all due to the breakage of the conjugated diene of ADDA group in MCs molecules, and the destruction of ADDA group usually means the detoxification of MCs. As has been pointed out by Acero [9], chlorination is feasible in removing MCs from drinking water without health risks if the pH value is kept below 8. Besides, the electrochlorination with BDD electrode offers more advantages over chlorination for the on-site generation of oxidants [31]. Although no hazardous byproducts in MC systems are detected so far, it is worthy to note that further studies needs to be extensively conducted to confirm the results so as to use the BDD technology for practical applications. Studies are underway to optimize the process under a variety of water quality conditions and at environmentally relevant concentrations.

4. Conclusions

(1) The feasibility of MC-RR removal by anodic oxidation on BDD electrode was studied in bulk electrolysis varying the operating and electrolyte conditions. It was observed that the full and quick removal of MC-RR could be obtained only in the presence of NaCl as electrolyte. The NaCl concentration and the applied current densities were listed as two most important operating variables, and all showed jumps in the oxidation abilities at a certain point under adjusting. A compromise between them must be reached, so as to attain the full destruction of MC-RR in a reasonable time and with an acceptable energy cost.

(2) Due to the similarity in molecular structure between various MCs, similar results may be speculated in the destruction of MC-LR and other MCs. Thus, all MCs presented in drinking water could surely be rapidly removed by anodic oxidation on BDD electrode without adding extra salts, which showed prospects of introducing BDD electrode to the household water purifier or large water supply in the near future.

(3) Summarizing the present state of research, the practice of combining BDD electrolysis with other options such as ultrasolysis, photocatalysis might be feasible in further improving the performance of the BDD technology, a more careful approach was still called for study.

Acknowledgments

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