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Removal of Chloramphenicol and Simultaneous Electricity Generation by Using Microbial Fuel Cell Technology

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The release of antibiotics into aquatic environments and its related long-term side effects have attracted great attention. As one of the most commonly used antibiotics in China, nitroaromatic antibiotic chloramphenicol (CAP) can be detected in aquatic environments. CAP removal efficiency in the anode chamber of microbial fuel cell (MFC) and the effect of CAP on the electricity output of MFC were studied in this paper. As compared to control experiments including open circuit MFC, no extra carbon source MFC, and abiotic MFC, the removal efficiency of CAP in normal MFC was the most outstanding. However, as the concentration of CAP increased, the removal efficiency is on the decline which is attributed to the CAP load increased. At an initial concentration lower than 30 mg L^{-1}, the electroactive biofilm-based MFC is robust with more than 95% voltage output maintained, but the voltage output dropped dramatically in antibiotic concentrations higher than 50 mg L^{-1}. An exponential relationship was found between the inhibition ratios of the MFC and the CAP concentrations in the studied concentration range. The findings about the CAP removal and the effects of CAP on the electricity output in two-chambered MFC in this work would have great importance to practical antibiotics wastewater treatment.

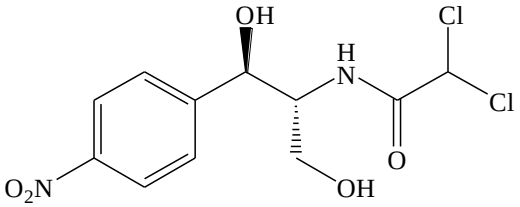
Keywords: Microbial fuel cell, Chloramphenicol, Bioelectricity generation, Removal

1. INTRODUCTION

Although antibiotics have been consumed for more than 60 years, their release and fate in the aquatic environment have been recognized as one of the most urgent questions in environmental sciences until the last few years [1]. An increasing number of reports are now available on the detection of antibiotics in various aquatic environments such as wastewater, surface waters, ground

water and so on. Besides the chemical pollution caused by antibiotics themselves, the use of antibiotics may also yield potential ramifications in the evolution of emerging antibiotic resistant bacteria and antibiotic resistant genes [2-4].

Chloramphenicol (2,2-dichloro-N-[1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl] acetamide, CAP) is a broad spectrum antibiotic, which is effective in treating infections caused by a wide variety of Gram-positive and Gram-negative bacteria. The chemical structure of CAP is:



Due to its genotoxic effect and severe side effects such as anemia, leucopenia, agranulocytosis, and aplastic anemia in some people [5], chloramphenicol is no longer recommended as first-line antibiotics to treat infections in developed countries. However, in developing nations chloramphenicol is still widely used. As one of the nine most common antibiotics used in China, chloramphenicol can be detected in surface and underground waters [6,7]. Therefore, many efforts are still needed to develop methods to degrade or to inactivate CAP in aquatic environments.

Recently the techniques based on photocatalytic degradation [8], Fenton process [9], and microwave radiation [10] were developed to eliminate CAP. Although, dechlorination or deactivation of CAP could be effectively realized by these methods, the drawbacks they presented could not be neglected such as high energy or chemicals consuming. Compared with other CAP removal strategies, bioelectrochemical systems (BES) have attracted increasing attention for their innovative advantages and environmental benefits such as higher degradation efficiency, lower maintenance cost, and more environmental sustainability [11, 12]. Wang and co-workers studied bioelectrochemical reductive degradation of CAP using BES with biocathode and applied voltage of 0.5 V. It was reported that the introduction of biocathode would better the cathode performance (compared with abiotic cathode), and then further increase the CAP reduction [6]. Based on intermediates analysis, they proposed the CAP cathodic transformation pathway and demonstrated that the antibacterial activity of CAP was completely removed and toxicity of CAP was efficiently reduced [13].

Microbial fuel cell (MFC) has become the most popular BES capable of generating electricity from various biodegradable organic substances using exoelectrogenic bacteria [14]. Compared to conventional anaerobic reactors, the degradation of organic contaminants were enhanced because that the anode of MFC could serve as a sufficient anaerobic terminal electron acceptor for microbes [15-18]. MFC is becoming a promising candidate for the removal of environmental contaminants and renewable energy generation in the past decade [19, 20]. Literature survey indicated that it is feasible to degrade antibiotics, for example, sulfonamides [21], ceftriaxone [22], tobramycin [23], and metronidazole [24] in MFCs. Since the explorations about utilizing MFC to achieve simultaneous electricity generation and antibiotics removal are still scarce. Therefore widely and exhaustive study in this field is highly necessary before practical application of MFC can be realized.

In this work, various experiments were conducted to explore the removal behavior of CAP in the anode chamber of MFC and to investigate the effect of CAP concentration on electricity output of MFC. Control experiments which were run in the open circuit MFC, no extra carbon source MFC, and abiotic MFC, were operated to compare CAP removal efficiency in the absence of current, extra easily biodegradable substrate, or metabolism of microbial, respectively.

2. EXPERIMENTAL SECTION

2.1 Design and configuration of MFC

Two-chambered MFC was constructed as our previously report with a slight modification [25]. The MFC reactors made of perspex material were consisted of two rectangular chambers with equal volume (7 cm×5 cm×4 cm, 140 mL), one is the anode chamber and the other is the cathode chamber. The reactors were constructed by bolting a cation exchange membrane (CMI-7000) between the two chambers with an external metal screw. In order to ensure the sealing between perspex walls and the membrane, rubber gaskets were used. Carbon papers (4 cm×4 cm, without waterproofing or catalyst) were used as anodes and cathodes. Before preparing electrodes, the carbon papers were sequentially soaked in acetone, 1 M HCl and 1 M NaOH for 4 h, 24 h and 24h to remove organics and other impurities. Titanium wires were used to connect the circuit with an external resistance of 1000 ohms. All leaks were sealed to maintain an anaerobic microenvironment in the anode chamber.

2.2 Inoculation and operation of MFC

The MFCs were inoculated with anaerobic sludge obtained from a Luotuowan wastewater treatment plant, Xinxiang, China. The anode growth medium solutions contained glucose (1000 mg L^{-1}, except for the co-substrate concentration experiments), 50 mM PBS (pH 7.0), vitamins and mineral as described previously [25]. The anode chamber was filled with the inoculated anaerobic sludge and the anode growth solutions at volume ratio of 1:3. CAP solutions with different concentrations were added according to the experiment design. During the start-up and acclimation stage, 1000 mg L^{-1} glucose in the anode growth solution was used as the sole fuel. When the electricity output of the MFC became stable, different concentrations of CAP (10, 20, 30, 50 and 80 mg L^{-1}, respectively) were added into the anode solution. The anode solution was replaced with fresh growth solution when the voltage decreased below 50 mV. N_2 gas was bubbled through the anode solution for 15 min to remove dissolved oxygen. In order to minimize the effect of the cathode on experimental results, 100 mM $K_3[Fe(CN)_6]$ in 50 mM phosphate buffer solution (pH=7.0) was used as the highly efficient electron acceptors [26, 27]. The MFC reactors were placed in the dark to prevent the effect of light. All MFC experiments were conducted at 30±1ºC in a constant temperature room. Three parallel groups of experiments were carried out to avoid the random errors caused by the biological fluctuation of the anaerobic sludge and other experimental conditions, and the average values of the results were taken.

In order to explore the impact of continuous current and physical adsorption on the removal of CAP in MFC, three groups of reactors (each group included three reactors) were randomly selected to start up and operate as the following control mode: open-circuit MFC: MFC reactor with the anode disconnected from the cathode, used as traditional anaerobic reactor; no extra carbon source MFC: MFC with no extra co-substrates (glucose in this work) added in the anode growth medium solutions; abiotic MFC: MFC with autoclaved anaerobic sludge used for inoculum.

The impact of electron transfer in MFC on the removal of CAP was investigated under open circuit conditions. Abiotic MFC and no extra carbon source MFC experiments were conducted to further prove the removal of CAP was mainly due to biocatalysis based co-metabolism degradation other than physical adsorption onto the anaerobic sludge, microbial cells and components of MFC reactors or the possible diffusion of CAP through the membrane to the cathodic chamber. All the comparison experiments were operated in batch-fed mode with the same experimental parameters. Sampling methods and the processing procedures for pretreatment and measurement were also set to be identical.

2.3 Analysis and calculations

Digital multimeters were used to measure the voltage output of MFCs every 30 min, and all the data can be automatically recorded by a computer. The external resistance was 1000 Ω except for the polarization curve experiment, which was conducted by changing external circuit resistance from 10,000 to 50 Ω.

The current density I_A (A m^{-2}) and the power density P_A (W m^{-2}) of the system were calculated using the equations: $I_A=V/(R\cdot A)$ and $P_A=V^2/(R\cdot A)$, where V (V) is the cell voltage, R (Ω) is the external resistance, and A (m^2) is the projected area of the anode.

An UV-vis spectrometer (Beijing Purkinje General Instrument Co., Ltd, China) was used for absorbance measurements. The maximum absorption band of CAP located at 278 nm in this work. When the reaction time was prolonged, the absorbance of the characteristic band decreased gradually, which reflected the successful elimination of CAP in the anode chamber. Removal of CAP was determined by monitoring the decrease in the absorbance at a wavelength of 278 nm. The anode solution was sampled every 2 h during every cycle with different concentration of CAP. Before measurement, sample solutions were centrifuged at 4,000 rpm for 15 min to remove suspended biomass from the anolyte and then filtered through a 0.22 μm-pore-size syringe filter unit. If needed, the sample solutions should be diluted with redistilled water before tests. The blank solution was taken from the MFC with no CAP added into the anode chamber, and the following pretreatment process was the same as that of the sample.

Removal efficiency was calculated as:

$$\text{removal efficiency}(\%) = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

A_0 is the absorbance of the solution sampled at reaction time t = 0 (min), and A_t is the absorbance of the solution sampled at certain reaction time t (min).

The inhibition ratio was calculated as:

$$\text{inhibition ratio}(\%) = \frac{V_{\max,0} - V_{\max c}}{V_{\max,0}} \times 100\% \quad (2)$$

$V_{max,0}$ is the maximal voltage in the batch without CAP addition, and $V_{max,c}$ is the maximal voltage in the batch with addition of CAP with certain concentration .

3. RESULTS AND DISCUSSION

3.1 Removal efficiency of CAP under different conditions

The removal and degradation of target pollutants are significant to the theoretical research and practical applications of wastewater treatment. In order to study the pollutant removal efficiency in normal MFC and the differences from open-circuit MFC, no extra carbon source MFC and abiotic MFC, comparison experiments are conducted to investigate the removal of CAP (30 mg L^{-1}). It is represented in Fig. 1 that the removal efficiency of CAP in normal MFC and in open circuit MFC reach up to 83.7% and 60.5%, respectively, whilst those in MFC with no extra carbon source and abiotic MFC display extremely poor removal performances, resulting in only 17.5% and 12.7%, respectively. Experimental results reveal that it is convincible to eliminate CAP using MFC reactors and the removal efficiencies of CAP in MFC are higher than that in any of the control experiments.

Firstly，although CAP can be efficiently removed in normal MFC and in open circuit MFC, the removal efficiency of CAP in normal MFC at any given time is higher than that in the open circuit during the 48 h test. The removal efficiency is approx. 60.5% during 12 hours in the MFC, whilst 47.3% is reached in the open circuit control and only 59.8% is achieved when the reaction time is extended to 48 hours. The accelerated removal of CAP in normal MFC reveals the important stimulation of the electron transfer for CAP removal. In a normal MFC, the anode and the cathode are connected to each other by an external resistor. The continuous electron transfer makes the anode a sufficient anaerobic terminal electron acceptor, which might have promotive effect on the metabolism of anodic functional microorganisms [22, 28]. While in open circuit control, no electron is transferred between the anode and the cathode, so the microbial electrochemical reactions are blocked or the metabolic rate of anaerobic bacteria decrease, which is likely to slow down the co-metabolism degradation of CAP [29].

Secondly, the lower removal efficiency in MFC with no extra carbon source or abiotic MFC indicates that the removal of CAP is mainly due to co-metabolism degradation based on biocatalysis other than physical adsorption and diffusion. The anaerobic co-metabolism of the CAP in MFC demands a readily degradable organic carbon source as a co-substrate to sustain microbial activities. Both the co-substrate and microorganisms are essential elements for efficient removal of CAP in MFC. Therefore, we suppose that the biocatalysis based anaerobic co-metabolism of CAP is probably the bioelectrochemical reductive degradation with CAP as the electron acceptor and the co-substrate (glucose in this work) as the electron donor. Our findings are in agreement with the results reported in previous literature that focused on the degradation of pentachlorophenol and azo dye [30, 31]. Although it has been demonstrated that CAP could be removed in the anode chamber of MFC, the

intermediate reactants has not been identified and the degradation mechanism is not clear. In our future work, we will focus our attention on study of degradation mechanism of antibiotics in MFCs.

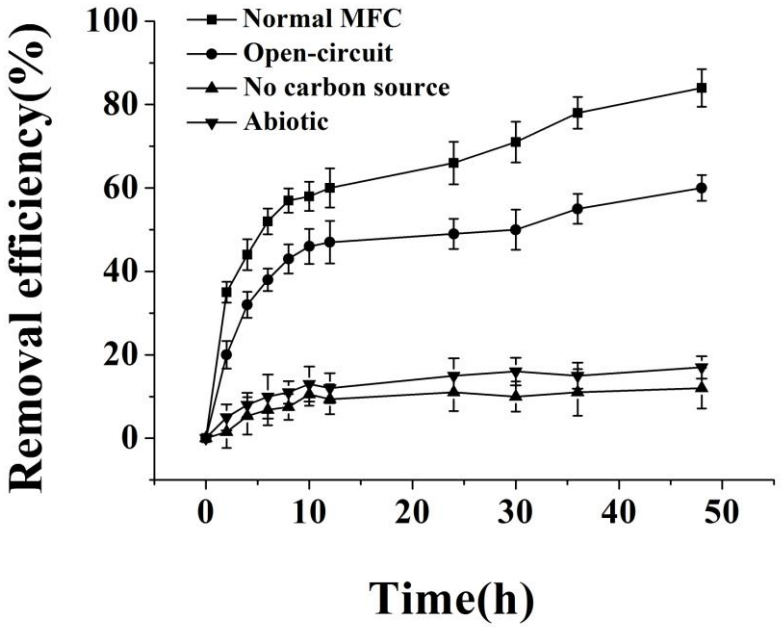


Figure 1. Removal efficiency of 30 mg L^{-1} CAP in normal MFC, open circuit MFC, no extra carbon source MFC and abiotic MFC.

3.2 Relationship between CAP removal efficiency and initial CAP concentrations

To investigate the influence of initial CAP concentrations on CAP removal performance, a series of anode solutions with different CAP concentrations (10, 20, 30, 50 and 80 mg L^{-1}) are added into the anode chamber of the two-chambered MFCs in successive operating cycles. CAP removal efficiencies are tested by measuring the UV-vis spectra during 48 h. It is noted from Fig. 2A that the removal percent decreases with an increase of initial CAP concentration during the 48 h experiment. Removal efficiency reached 90% at a lower CAP concentration of 10 mg L^{-1} in 48 h. Further increasing the CAP concentration to 20 and 30 mg L^{-1}, the removal efficiency of CAP slightly declines to 87% and 84%. At 50 mg L^{-1} of initial CAP, the removal efficiency of CAP has an obvious decrease (75% within 48 h). Even at higher concentrations of 80 mg L^{-1}, CAP removal is not strongly inhibited, 61% of the antibiotics could still be removed from the anode solution in 48 h. This interesting phenomenon may be attributed to the following two reasons: (1) increasing the CAP loading simply requests excessive reaction time to let the antibiotics to be treated; (2) the increasingly toxic effect on the bacteria may diminish the removal activity to some extent as the CAP concentration increases.

To better explain the trend generated in our investigation, CAP removal rate (the absolute amount of removed CAP per hour) is calculated and the results are depicted in Fig. 2B. The CAP removal rates are 0.026, 0.051, 0.074, 0.109 and 0.14 mg h^{-1} when the initial concentrations of CAP added into the anode chamber are 10, 20, 30, 50 and 80 mg L^{-1}, respectively. The absolute amount of removed CAP per hour increases with the growing initial concentration of CAP. Therefore, we

speculate that the decrease of the removal efficiency with an increase of CAP concentration is mainly attributed to the CAP loading effect, and the anodic microbial community shows a high degree of toxic tolerance to CAP in the studied concentration range.

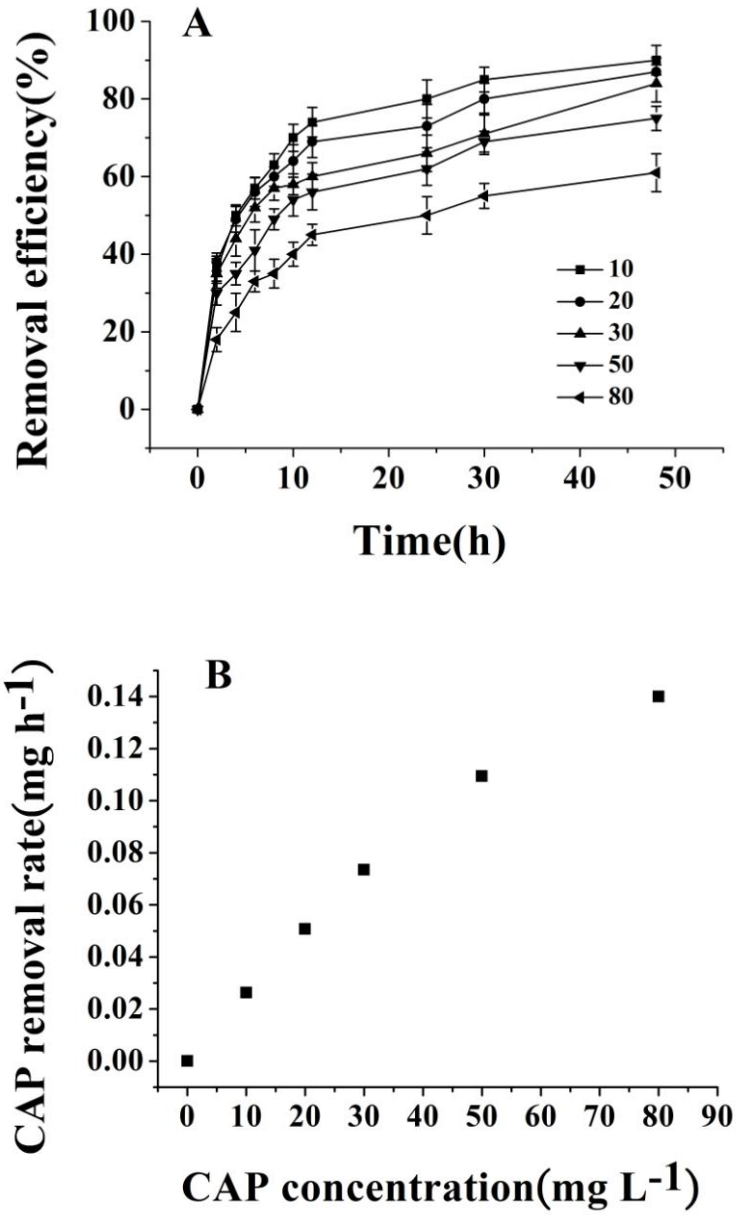


Figure 2. (A) Effect of the initial concentration (10, 20, 30, 50, 80 mg L^{-1}) of CAP on the removal efficiency; (B) The relationship between CAP removal rate and the initial CAP concentration in the anode chamber of the two-chambered MFC.

3.3 Effects of CAP on the performance of MFC

As an innovative technology for wastewater treatment, MFC has attracted much attention because electricity can be generated while degrading organic compounds in wastewater. In order to investigate the simultaneous bioelectricity generation performance of MFCs during the process of CAP

removal, output voltage of the MFCs supplied with 1000 mg L^{-1} glucose and CAP in the concentration range from 10 to 80 mg L^{-1} are measured as a function of operation time. One of the representative cycles is presented in Fig. 3A.

Stage a is the start-up stage with 1000 mg L^{-1} glucose as the sole substrate. After inoculation, the maximum voltage ascends from 185.1 mV in the first cycle to 567.8 mV in the third cycle. During the fourth circle, the peak voltage starts to stabilize at 560±10 mV. The repeatable and steady output voltage indicates that exoelectrogenic bacteria are grown and adhered on anode surface and marks the accomplishment of the MFC start-up stage.

During stage b, cultivation solutions containing 1000 mg L^{-1} glucose and different concentrations of CAP are added into the MFC as mixed substrates. At concentrations of 10 and 30 mg L^{-1}, there is no obvious immediate voltage decrease after addition of CAP, almost 95% voltage output can be maintained. The stable voltage output with CAP concentrations lowering than 30 mg L^{-1} indicates that this level of CAP concentration is within the range of adaptation of electrochemically active bacteria in the biofilm. The results also demonstrate that compared to planktonic cells, wastewater-derived electroactive biofilms show less susceptibility to toxins [23, 32]. Obvious inhibition of electricity output is observed at 50 mg L^{-1} CAP, and the inhibition is further enhanced as the concentration reaches up to 80 mg L^{-1}, only 75% voltage output can be kept. The experimental results are probably owing to the following reasons: (1) electron competition. There would be a competition between the reductive degradation of CAP and the anode. High concentration of CAP added into the anode chamber would consume more electrons for reductive degradation, and then fewer electrons are transferred to the anode for electricity generation, which would be the possible reason for the decrease of power output. (2) Activity repression of exoelectrogenic bacteria by the toxicity of CAP and the possible composition change of the active microbial communities would also be considered as sound reasons for the voltage decrease in MFC.

Stage c is the recovery stage with 1 g L^{-1} glucose as the sole substrate. The maximum voltage output can gradually recovers by replacing the anodic solution three times. These results suggest that some microbial species directly or indirectly relating to bioelectricity generation in the biofilm could probably be recovered from those community members who are not killed at the given antibiotic dose and exposure time [23]. Polarization curves and power density curves are obtained by varying the external resistance to characterize the power output of MFC at various concentration of CAP (Fig. 3B). The curves corresponding to 10, 20 and 30 mg L^{-1} CAP interlace with one another. Therefore, in order to plot the figure more clearly, only the curves at CAP concentrations of 0, 30, 50 and 80 mg L^{-1} are plotted.

With the external resistance varying from 10,000 to 50 Ω, the MFC without adding CAP in the anode chamber generates a maximum power density of 289 mW m^{-2} at the current density of 951 mA m^{-2}. When the mixture of 1000 mg L^{-1} glucose and 30 mg L^{-1} CAP was used, the maximum power density decreases by 22%, to 223 mW m^{-2} at the current density of 873 mA m^{-2} (drop by 27% and 30% for 10 and 20 mg L^{-1} CAP). When 50 mg L^{-1} of CAP is added, the maximum power density decreases to 128 mW m^{-2} at the current density of 517 mA m^{-2}, which is 55% lower than that obtained from MFC without CAP. Increasing the CAP concentration to 80 mg L^{-1} further decreases the maximum power density by 70%, resulting in 86 mW m^{-2} at the current density of 408 mA m^{-2}. The

results of polarization experiments further verify that at lower concentrations of CAP (lower than 30 mg L^{-1}), 70%-80% electrical power can be maintained with simultaneously efficient removal of CAP. But the presence of CAP with relatively high concentrations (higher than 50 mg L^{-1}) can exert obvious negative effects on MFC power generation.

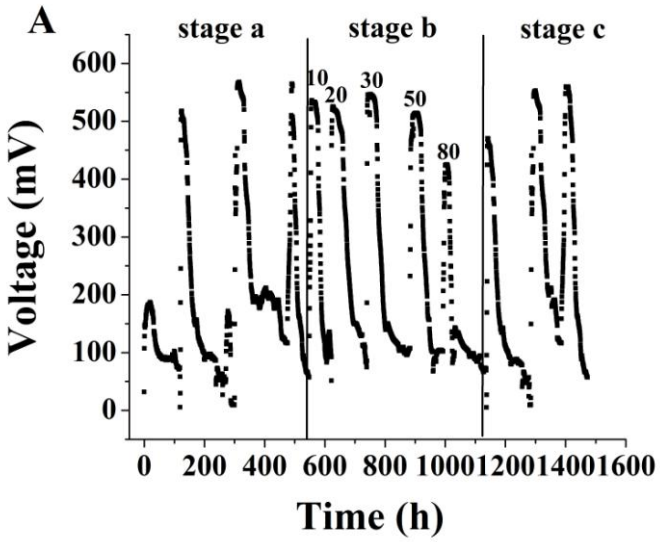


Figure 3A. Voltage output of MFC. The substrate for stages a and c: 1 g L^{-1} glucose; the substrates for stages b: 1 g L^{-1} glucose with different concentrations of CAP (10, 20, 30, 50 and 80 mg L^{-1}). External resistance: 1000 Ω.

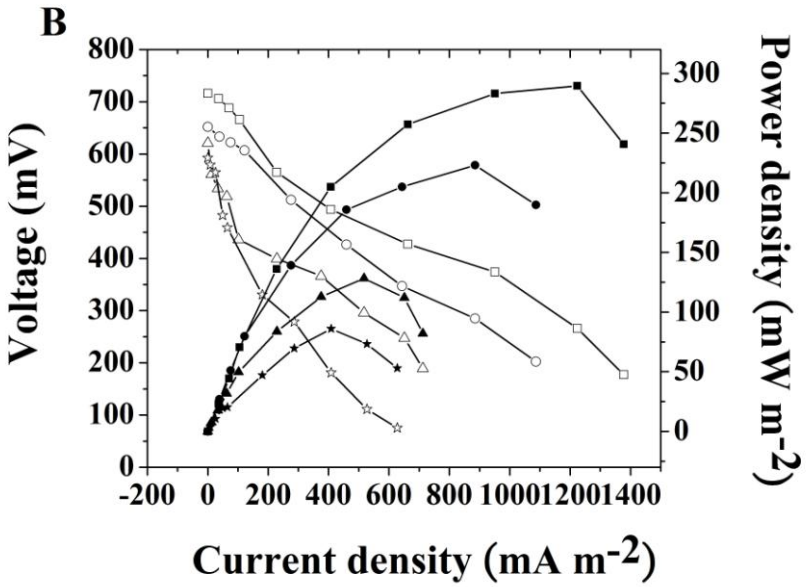


Figure 3B. Polarization (hollow symbol) and power density (solid symbol) curves of MFC with 1 g L^{-1} glucose containing different concentrations of CAP (0■, 30●, 50▲and 80★mg L^{-1}).

3.4 Inhibition ratio of MFC with CAP concentrations

In order to further explore the effect of CAP on the electroactive biofilms and the power output of the MFC, the inhibition ratios of MFCs with different CAP concentration in terms of the changes of

the output voltage was calculated. The inhibition ratio fluctuates between 5.1% and 7.2% when the initial CAP concentration varies from 10 mg L^{-1} to 30 mg L^{-1}. Then, the inhibition ratio of CAP drastically increases from 5.1% to 24.9% as the antibiotic concentration ascends from 30 mg L^{-1} to 80 mg L^{-1}. Furthermore, Fig. 4 displays that the inhibition ratio has an exponential relationship with the initial CAP concentration. The regression equation is:

$$y = 0.208e^{x/17.6} + 5.32 \qquad R^2 = 0.98718$$

The exponential relationship indicates that the reaction occuring on the anode of the MFC would be a combination of biofilm kinetics and electrochemical kinetics. A possible explanation for the non-linear correlation between CAP and inhibition ratio is probably the changing of kinetic inhibition of microorganisms in the biofilm [23, 33].

Antibiotics, detected in surface waters and wastewaters, are always at levels of μg L^{-1} [34]. To the best of our knowledge, the reported maximum concentration of CAP in aquatic environment was 47.4 μg L^{-1} in Asian countries including China [35]. Based on the inhibition ratio values we test and the actual antibiotic concentration detected in aquatic environment, we deduce that the functional microbial community based MFC may be applicable as a water treatment technology.

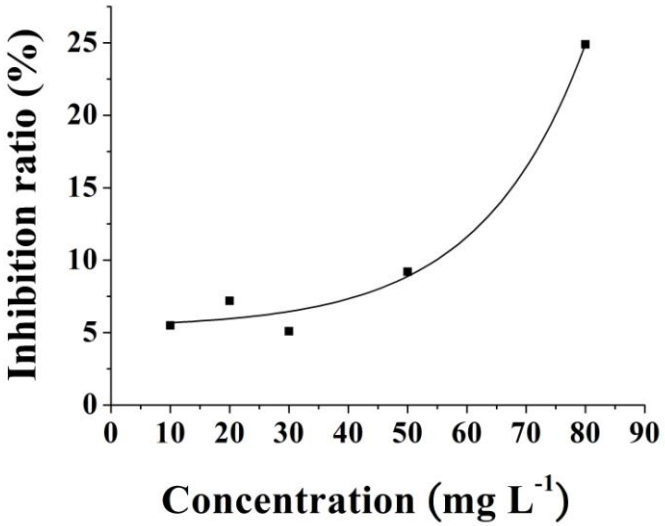


Figure 4. The exponential relationship between inhibition ratio and the initial CAP concentration.

4. CONCLUSIONS

Simultaneous CAP removal and bioelectricity generation is achieved using glucose as the co-substrate in two-chambered MFCs. The higher removal efficiencies in normal MFC than that in any control experiments indicate that the removal of CAP is mainly due to biocatalysis based co-metabolism degradation. The removal efficiency gradually decreases with the increased CAP concentration because of the increased antibiotics loading. The power output shows a high degree of robustness against CAP at concentrations lower than 30 mg L^{-1} and decreases sharply as the CAP concentration arrived at 50 mg L^{-1}. The voltage output inhibition ratio has an exponential relationship

with the initial CAP concentration. Our results indicate that it is feasible to realize antibiotics removal with simultaneous bioelectricity generation in MFC, which may present a novel method for antibiotics wastewater treatment.

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