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Degradation of Chloramphenicol with Novel Metal Foam Electrodes in Bioelectrochemical Systems

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Abstract

Bioelectrochemical system (BES) has been considered as one of the efficient methods for recalcitrant organic pollutant removal. This study compared three different cathodes, i.e. carbon rod (CR), copper foam (Cu), nickel foam (NF), for chloramphenicol (CAP) removal in BESs, while Cu and NF have not been used as cathodes for CAP degradation before. The results demonstrated that with 0.3 V applied voltage, 100% removal of 32 mg L\textsuperscript{-1} CAP was observed after 36 h and 24 h with CR and Cu electrodes respectively, while amines were the main intermediate products. The performance of Cu cathode was 15.13 times better than NF electrode under 0.3 V applied voltage. When the applied voltage increased to 0.5 V, CAP could be completely removed within 12 h with Cu electrode, while complete CAP removal was found after 24 hours for CR and more than 120 hours for NF respectively. With 0.5 V applied voltage in 24 h degradation period, the final degradation products were found to be CO\textsubscript{2} and H\textsubscript{2}O for Cu electrode, while nitrobenzene and 4-Nitrobenzyl alcohol were the main products for CR and NF electrodes respectively. The results demonstrated that Cu was the most efficient cathode for CAP degradation.

Keywords: Chloramphenicol; Bioelectrochemical systems; Metal foam electrodes; Degradation mechanism
1. Introduction

Widespread of antibiotics in the open environment has become an emerging concern in recent years [1]. A variety of antibiotics were detected in pharmaceutical manufacturing wastewater [2]. The wastewater, once entering the environment, will impose a potential environmental risk and threaten human health. Among the commonly used antibiotics, chloramphenicol (CAP) is a popular antibiotic compound for human and animals due to its excellent antimicrobial properties and low price [3, 4]. It has a broad-spectrum and can effectively deactivate most of Gram-positive and Gram-negative bacteria [5, 6]. Therefore, many researchers have looked into their impact on the environment and explored the methodologies to effectively remove this compound.

It was reported that chlorinated nitro aromatic antibiotics could be removed by conventional biological wastewater treatment system with a long solids retention time (SRT) (10-70 days) [7, 8]. However, the degradation cannot be completed and 4-nitromandelic acid, 4-nitrobenzyl alcohol, 4-nitrobenzoic acid, 4-aminobenzoic acid, are commonly found in the treated effluent, and long SRT also leads to sludge accumulation [9]. On the other hand, electrolysis can reduce CAP efficiently and completely, while the high energy consumption is a major concern to deploy such technology [5].

CAP can exhibit reduction peak current when the potential is below -0.4 V in electrochemical test [10], hence microbial electrolysis cell (MECs) with a 0.5 V applied voltage have been explored for CAP reduction [3, 10-13]. Lower applied voltage has not been tested according to our best knowledge. In most of these studies,
conventional carbon-based materials, e.g. carbon rod, carbon fiber, graphite felt, carbon cloth, graphite blush, were selected as cathodes. In spite of non-corrosive and biocompatibility characteristics of carbon materials, the conductivity is not as good as metal materials [14]. Metal materials are commonly used in some conventional electrolysis process to enhance electrochemical catalytic activity [15, 16]. Compared to normal metal electrodes, metals foam has highly open porous walls and larger specific surface area [17, 18]. The unique characteristics of metal foams can accept the electrochemical deposition. The excellent performance of copper nanofoams in the CO₂ reduction in an electrochemical cell indicated that the high surface roughness, hierarchical porosity, and confinement of reactive species of the material contributed to both final products and faradaic efficiencies [18]. Nickel foam as the cathode was studied in an electrocoagulation device for boron removal and results revealed nickel foam removed 99.2% of 10 mg L⁻¹ boron acid in 120 min at particular onset potential of 0.8 V [19]. Nickel foam has also been considered as the best cathode material for hydrogen generation [20].

In this study, for the first time, the metal foam was used as the cathode to degrade toxic and recalcitrant organic compounds in a bioelectrochemical system. CAP was chosen as a model antibiotic to investigate the efficiency of carbon rod, copper foam and nickel foam as electrodes. The effect of applied voltage and electrochemical activity of these materials were elucidated by cyclic voltammetry (CV) test and electrochemical impedance spectroscopy (EIS). The degradation mechanism of CAP in the electrochemical oxidation system was analyzed and a
possible degradation pathway of CAP was proposed.

2. Methods and materials

2.1 Reactor setup

All bioelectrochemical reactors were made of dual cubic chambers, which were separated by a cation exchange membrane (Ultrex CMI-7000, Membranes International, Ringwood, NJ, USA). The working volume of each chamber was 28 mL. A carbon rod (CR, Chijiu Duratight Carbon Co., China) and graphite fiber (1.5×1.5×1.0 cm, Sanye Co., Beijing, China) were used as the anode electrode. During the acclimation period, carbon rod was also used as the cathode electrode. Carbon rod (CR, diameter of 0.8 cm, length of 3.2 cm), copper foam (Cu, 2.0×2.0 cm, 99%, Jiashide Co. Suzhou, China) and nickel foam (NF, 2.0×2.0 cm, 99.9%, Jiashide Co. Suzhou, China) were applied as cathode materials for comparison during experiment stage. The working area for all these three cathode electrodes was 8 cm². During the electrochemical tests, all current density were normalized by the working area of electrodes. These materials were cleaned before tests using 0.5 M H₂SO₄. Three reactors with different cathodes were operated in parallel to compare the performance of CAP removal. All reactors were operated under open circuit condition with different applied voltage (0.3 V and 0.5 V in sequence).

2.2 Inoculation and operation

The microbial community in anode chambers was inoculated from a
bioelectrochemical reactor with acetate as feed [21, 22]. The anolyte composed of (g L\(^{-1}\)) sodium acetate, 1.0; KH\(_2\)PO\(_4\), 4.4; K\(_2\)HPO\(_4\), 3.4; NH\(_4\)Cl, 1.3; KCl, 0.78; MgCl\(_2\), 0.2; CaCl\(_2\), 0.0146; NaCl, 0.5; trace vitamins and minerals [23-25]. The feed was sparged with N\(_2\) for 15 min before fed into the anode chamber. During anode acclimation period, DI water with dissolved oxygen was used as electrons acceptor in cathode chamber [14], and an external resistor of 1000 \(\Omega\) was used [23]. After eight-cycle feeding, the catholyte was replaced by aqueous CAP (32 mg L\(^{-1}\), pH = 6.0 and 3.83 \(\pm\) 0.04 mg L\(^{-1}\) dissolved oxygen). The pH and conductivity of catholyte were adjusted with 1 M HCl and 1 M NaCl respectively.

Microbial fuel cell (MFC) mode was applied during the acclimation period. From day 18, three reactors were operated under applied voltage of 0.3 V (MEC mode) to investigate the removal efficiencies. In order to compare the performance with the literature [10], a higher applied voltage of 0.5 V, which was commonly used for CAP degradation, was investigated from day 30 to day 60. Open circuit conditions (OCCs) as control experiments for three cathodes were carried out separately to examine changes of CAP in the absence of current generation. All reactors were operated in fed-batch mode and maintained at room temperature. All experiments were carried out in duplicates.

2.3 Measurements and analysis

Total chemical oxygen demand (COD) in the anolyte was determined according to the standard method [22, 26]. Total organic carbon (TOC) was analyzed by a TOC
auto analyzer (Shimadzu TOC-VCPH; Japan). Solid-phase extraction (SPE) (Strata-X, Phenomenex Co. Singapore) was conducted to detect CAP degradation products. After filtered through 0.22 µm filter, the purified samples were analyzed by a High-Performance Liquid Chromatography (HPLC 1260, Agilent) coupled with a C18 column (Gemini-NX 3µ, 110A, 100×2.0 mm, Phenomenex). The mobile phase was methanol and water (55/45; V V⁻¹). The eluent was delivered at a flow rate of 0.3 mL min⁻¹ and the absorbance at 275 nm was measured. To identify the products of CAP degradation, LC-MS/MS (G6460C, Agilent) equipped with an electrospray ionization source were used. The LC/MS was operated under negative [27] polarity mode with the same C18 column. The mobile phases were gradient distilled water and acetonitrile with 0.1% acetic acid, at a 0.25 mL min⁻¹ flow rate. The scanned range was from 60 m/z (mass to charge) to 400 m/z.

An automatic data collection system (PISO-813, Hongge Co., Taiwan) was used for collecting potential of anode and cathode. The power density of microbial cells was tested with a potentiostat (SP-150, BioLogic, Singapore) using the anode as a counter electrode and cathode as the working electrode. Before the linear sweep voltammetry measurement, the cell was in open circuital mode until the potential was stabilized and then tested from 0.0 V to the open circuital potential (OCP) at a scan rate of 0.1 mV s⁻¹ [23]. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests for cathode were conducted with the same potentiostat. A three-electrode system using cathode electrode as working electrode, an Ag/AgCl as the reference (195 mV vs. SHE) near the working electrode and a Pt filament as a
counter electrode was set-up for EIS and CV tests. The Pt filament was used to replace the anode biofilm to avoid any possible effect of anode bacteria on the analysis of the cathode. During the analysis, the anolyte was 50 mM PBS buffer solution while the catholyte was 32 mg L\(^{-1}\) CAP solution. The electrodes were characterized electrochemically by CV tests in a NaCl solution without (same conductivity as 32 mg L\(^{-1}\) CAP) and with 32 mg L\(^{-1}\) CAP. EIS analysis was conducted under polarized conditions, which was close to MFC cathodic operating potentials of -0.1 V and 0 V (vs. SHE, for different cathodes), with a frequency range of 100 kHz to 1 mHz and a sinusoidal perturbation of 10 mV reference amplitude[28]. The equivalent circuit and detailed value of different resistances were conducted through Zsimpwin software [29].

2.4 Calculation

Reduction efficiency of CAP in MEC, anodic coulombic efficiencies (CE\(_{an}\)), reaction rate constant \(k\) (h\(^{-1}\)), half-life time (t\(_{1/2}\)) and overall system efficiency for CAP degradation (mol CAP mol\(^{-1}\) ΔCOD) were calculated using Eqs. (1)-(5):

\[
\text{CAP reduction} \ (\%) = \frac{\text{CAP}_i - \text{CAP}_f}{\text{CAP}_i} \times 100\%
\]  

(1)

\[
\text{CE}_{an} = \frac{\sum_{i=1}^{n} I_i \Delta t}{F \times 4 \times \Delta \text{COD}_{an} \times V_{an} \times M_{\text{O}_2}} \times 100\%
\]  

(2)

\[
C_i = C_0 e^{-kt}
\]  

(3)

\[
t_{1/2} = \frac{0.693}{k}
\]  

(4)
η_{CAP} = \frac{[CAP_i - CAP_t] \times V_{MEC,an} \times M_{O_2}}{\Delta COD_{MECan} \times V_{MEC,an} \times M_{CAP}} \tag{5}

Where \(CAP_i\) is the initial concentration in the catholyte whereas \(CAP_t\) is the concentration at an operation time of \(t\) (mol L\(^{-1}\)); \(V_{MEC,an}\) and \(V_{MEC,ca}\) are anolyte and catholyte volumes in the MEC respectively (L). \(\Delta COD_{MECan}\) is the cumulative COD consumptions over a set period of \(t\) in the anodes of MEC (g L\(^{-1}\)); \(I\) is circuit current (A); 32 is the atom/molecule weight of O\(_2\); 4 is the molar number of electrons required for oxygen reduction (mol mol\(^{-1}\)); \(F\) is the Faraday constant (96485, C mol\(^{-1}\) e\(^{-}\)).

3. Results and discussion

3.1 Comparison of CR, Cu and NF reactor performance under 0.3 V applied voltage

During acclimation period, reactors were in MFC mode, where dissolved O\(_2\) was cathodic electrons acceptor. In initial five cycles, feed medium was mixed with anode effluent from a stable MFC reactor to accelerate the enrichment of exoelectrogens. After several cycles, the potential in MFC experienced a gradual decrease (Fig. 1A). From day 10 onwards, feed medium only was used and the potential of anode further decreased from -0.25 V to -0.3 V. These values are frequently observed with 1 g L\(^{-1}\) acetate as anodic fuel in MFC [30]. The results clearly demonstrated the development of biofilms on anode electrode was successful and the biofilms were matured after 5-6 cycles. From day 18, DI water in cathode chamber was replaced with 32.57 ± 0.62 mg L\(^{-1}\) CAP solution and the reactor was converted to MEC with applied 0.3 V voltage. As such, a sharp decrease of the cathode potential was observed (Fig. 1A). The
potential appeared stable in the following three cycles’ operation (Fig. 1A),
demonstrating the suitability of the MEC for further experiments.

In the open circuit test, only around 7.8% of CAP was removed during 120 h
operation regardless of cathode type (Fig. 1B). Therefore, electrons generated from
the anode and applied voltage can certainly enhance the degradation efficiency (Fig.
1B). With 0.3 V applied voltage, 88.68% of CAP was removed in MEC using NF
cathode after 120 h. The circuit current density of NF cathode was 4.91 ± 1.82 A m⁻³
(Fig. 1D). The average cathode potential of NF was about -0.37 V (Fig. 1C), therefore
hydrogen evolution may contribute as a electrons competitor in such system [20].
Different from NF performance, CR completely degraded CAP in 36 h with \( \eta_{\text{CAP}} \) of
0.36 mol CAP mol⁻¹ ΔCOD and Cu completely removed CAP in 24 h with \( \eta_{\text{CAP}} \) of
0.54 mol CAP mol⁻¹ ΔCOD respectively (Table 1). The higher current density of
11.01 ± 4.07 A m⁻³ with Cu (Fig. 1D) may contribute to the higher removal efficiency.
In addition, the rate constant \( k \) of Cu cathode was 1.75 and 16.13 times to that of CR
and NF cathodes (Table 1), indicating that copper foam electrode had better
degradation performance. Moreover, a higher CE_{an} of Cu further confirmed that Cu
was a more efficient material for CAP degradation. It was also understandable the
more negative Cu cathode potentials of -0.52 V to -0.59 V (Fig. 1C) led to higher
CAP degradation. These results demonstrated the importance of cathode materials
selection on efficient CAP reduction in MEC.

3.2 Comparison of CR, Cu and NF reactor performance under 0.5 V applied voltage
It was clear that the reduction efficiency of CAP by CR, Cu and NF cathodes increased with higher applied voltage (Table 1). Notwithstanding, the efficiency of NF cathode was always lower than the other two materials with the consequence of the lower current density (Fig. 2C). With higher applied voltage of 0.5 V, CAP degradation by NF cathode increased to 94.88% in 120 h, higher than the removal efficiency of 0.3 V condition (Table 1). The higher removal efficiency of CAP under 0.5 V was due to the lower cathode potential and higher current density at higher applied voltage (Fig. 2). However, as an excellent cathode material for hydrogen evolution, nickel foam can benefit from the more negative cathode potentials at higher applied voltages for hydrogen evolution rather than CAP degradation [20, 31]. In addition, there was a general increase trend of the cathodes potential for these three cathodes under higher voltage (Fig. 2B), consistent with the tendency of circuit current (Fig. 2C). These results were in agreement with the previous study that higher circuit current led to higher over potential for hydrogen ion reduction [32, 33].

The three cathodes exhibited different overall efficiency ($\eta_{\text{CAP}}$) and CE$_{\text{an}}$ increased with the increase of corresponding circuit current in most cases (Table 1), mainly ascribed to the trend of anodic COD consumption (Eqs.2). The copper foam had higher overall efficiency at both applied voltage (Table 1). After 6 h, there was only 1.46 ± 0.28 mg L$^{-1}$ CAP left in the effluent from Cu reactor under 0.5 V. However, lower anodic columbic efficiency was observed for Cu. This is the consequence of high COD consumption under higher applied voltage [20, 34]. At the same applied voltage of 0.5 V, the copper foam had a higher rate constant of 0.571
than that of carbon material based bio-cathode [10]. In addition, the XRD curves confirmed that CR and NF electrodes were very stable after 120 h operation, while a very small area of Cu electrode was oxidized to CuO likely due to the natural oxidation in the atmosphere during sample transportation and analysis (Fig. S1). Hence, there is a great potential for copper foam to replace conventional bio-cathode for CAP degradation due to the lower cost, better performance and stability.

3.3 Voltammetric characteristics of cathodes using CV

The CV curves for these electrodes were recorded between -1 to 0.5 V (vs. SHE) at a scan rate of 10 mV s⁻¹. In the catholyte of BESs, oxygen, due to the high redox potential, can easily obtain electrons from the electrode. Oxygen reduction reaction (ORR) involves a series of electrons transfer processes which depend on the type of electrodes materials. In general, the reduction of oxygen in electrolysis process occurs through either two electrons or four electrons pathway [8]. The oxygen molecules approaches electrode through the diffusion transport, so adsorption preference of electrode materials towards oxygen may affect the preponderance of these two pathways [9]. CV tests can provide an effective way to analyze the ORR on the three electrodes and further reveal the mechanism of CAP degradation in BESs [10].

In the presence of oxygen without CAP, Cu and NF electrodes showed double reduction peaks at -0.12 V and -0.43 V respectively which demonstrated the oxygen was reduced through these two pathways on these metal foam electrodes (Fig. 3B). The two electron pathway is beneficial for the further formation of radials [9].
However, CR as cathode only displayed one reduction peak near -0.20 V (Fig. 3B) that indicated the oxygen reduction was carried out through the four electron pathway with conventional carbon electrode [10]. Under the same electrolyte conditions, Cu electrode had a higher reduction peak current (Fig. 3B) which demonstrated this material had more catalytic characters for the ORR [11]. In the absence of oxygen, compared with the blank control, CAP exhibited reduction peak on these three electrodes at -0.40 V (Fig. 3A and Fig. 3B) which indicated the CAP could obtain electrons through electrodes directly [12].

In the presence of both oxygen and CAP, these three electrodes showed ORR peak near -0.12 V and CAP degradation peak near -0.40 V (Fig. 3A), which suggested during the CAP degradation, oxygen was involved in the two electrons pathway and producing radicals [8]. This also corresponded with the observed hydrolysis product that had molecular mass of 339 (Fig. 5). As shown in Fig. 3A, when 32 mg L⁻¹ CAP co-existed with the dissolved oxygen, a strong reduction current peak of -10.74 mA for copper foam was observed at -0.606 V (Fig. 3A). Compared to CR and NF electrodes, Cu exhibited higher reduction current. NF had the lowest reduction current at about -0.52 V, corresponding to the relatively poor performance for CAP degradation. The results strongly suggested that the removal efficiency of CAP was highly dependent on the materials reduction current. In addition, NF, as an excellent material for hydrogen generation, exhibited a hydrogen reduction peak near -0.79 V (Fig. 3A). This hydrogen generation process competed electrons with CAP degradation, leading to the lowest performance of NF (Fig. 2A) [6].
In order to further investigate the limiting factor of the electrolysis, copper foam as the most efficient cathode in this study was chosen as the electrode to test CV under different scan rates varying from 1 mV s\(^{-1}\) to 10 mV s\(^{-1}\). The effect of different scan rates on the voltammetric response of Cu electrode was investigated and the results are shown in Fig. 3C. It is clear that the redox couple in all cyclic voltammograms exhibited an increased current response with the increase of scan rate from 1 to 10 mV s\(^{-1}\). Fig. 3D showed that the peak currents were proportional to the square root of the scan rates. The peak current was linearly with the square root of scan rate, reflecting that the redox reactions on the Cu electrodes were the typical electrons acceptor diffusion-controlled electrochemical processes [5]. Such diffusion limited the speed of electron transfer, as evidenced by the strong correlation between soluble CAP concentration and anodic current [39]. Diffusion limits the contribution of electron transfer by this mechanism, as shown by the strong relationship between soluble CAP concentration and anodic current [39].

### 3.4 Electrochemical analysis of cathodes using EIS

Based on the same anode, EIS was used to explore the main reason for the different performance of these three materials. EIS spectra were fitted to equivalent circuits (Fig. 4A) to identify the components of the internal resistances of the cathode material. After EIS test, the fitting circuit nyquist data were fitted using the electrical circuit given in Fig. 4A, with representative parameters for the polarization and ohmic resistances, which delineate the resistance of materials [40]. As described in Fig. 4B
of the fitting results, copper foam electrode exhibited a lower electrode ohmic resistance (37.6 Ω) and electron transfer resistance (45.4 Ω) than CR and NF. The lowest resistance of Cu electrode exhibited the highest circuit current (Fig. 1D and Fig. 2B) which contributed to the higher degradation efficiency of CAP.

3.5 Degradation pathway of CAP

CAP degradation products were identified by LC-MS. The major intermediates products were mono- and di-hydroxyl derivates of CAP (Fig. 5), which are the typical products from electrolysis or photodegradation processes [5, 27]. It is speculated that electrochemical degradation of organic pollutants was recognized as a free-radical mechanism where hydroxyl radicals (·OH) or ·O₂⁻ formed on the electrode. On the cathode, the electrons generated by the anode transferred to the surface of the material and then scavenged by dissolved oxygen, facilitating the hole–electron separation. Meanwhile, the holes leaving from the valence band of the cathode to form hydroxyl radicals or directly oxidize various organic compounds [41].

According to the detected products at different sampling points, CAP degradation pathways with different cathodes were proposed. Under 0.3 V applied voltage, there were two possible pathways for CAP degradation using Cu and CR as cathodes, whereas the pathway using NF was straight forward (Fig. 7). For NF electrode, the starting change was the hydroxylation of the head-end carbon with a nitrato nitro-group, yielding the compound M1, ion with m/z 309 [M–H]⁻, which was consistent to the addition of mass to CAP. The degradation ceased in the form of M1.
due to the lower current and high cathode potential (Fig. 1C and Fig. 1D). For CR and Cu cathodes, the initial degradation started from the hydroxylation of the terminal carbon that contains two chlorine atoms to form compound M2. The presence of M3 was due to the reaction of M2 who accepted six electrons [10]. Two side chains of M3 were detached and benzene ring formed via hydroxyl radicals attack. Then the further hydroxyl radicals attack would result in the formation of CO₂ and H₂O. For these three materials, M9 was also detected as the common hydrolysate.

After changing applied voltage to 0.5 V, potential below -0.6 V was achieved for all three cathodes. The degradation started directly from the bond breaking of the terminal carbon that contains two chloride atoms, yielding the compound M3, ioned with m/z 237/239 [M–H]⁻. Further oxidation of the amino and hydroxyl groups of M3 led to the production of M5. Subsequent oxidation of the lateral groups of M5 broke the side chain of the methyl to produce nitrobenzene. The denitration of nitrobenzene yielded M7 by obtaining six electrons. This compound was ultimately converted to CO₂ and H₂O with further hydroxyl radicals attack. Similar behavior was observed during the photolytic degradation of the antibiotic sulfamethoxazole [27].

The results confirmed that different cathode materials exhibited different cathode potential and circuit current which in turn affected the degradation pathways and removal efficiency of CAP. Compared with the conventional semiconductor heterojunction photocatalysts or electrolysis processes, copper foam as the cathode of BES achieved high CAP removal efficiency in situ with the electrons generated from anode and also this non-coated material can greatly reduce the cost. With the Cu
cathode, the relatively lower cathode potential would be sufficient to achieve more complete degradation of CAP.

4. Conclusions

In this paper, bioelectrochemical degradation of chloramphenicol (CAP) in aqueous solution was investigated using carbon rod (CR), copper foam (Cu) and nickel foam (NF) as cathodes. Based on the comparison of degradation performance, applied voltage, electrochemical activity of these materials, it could be concluded that:

(a) Copper foam had the best performance for CAP degradation. The electrochemical degradation of CAP on Cu electrode followed pseudo-first-order kinetics. The degradation and mineralization ratios of 32 mg L⁻¹ achieved complete removed within 12 h with Cu electrode under 0.5 V applied voltage. Copper foam is a promising material as the cathode for recalcitrant organics degradation in wastewater treatment.

(b) Applied voltage was the most important factor in determining degradation and mineralization efficiency. The increase of applied voltage contributed to the higher circuit current and complete degradation of CAP.

(c) The degradation mechanism was proposed based on cyclic voltammetry tests and it was deduced that electrons generated from anode microorganism and the hydroxyl radicals generated in the cathode played key roles in reducing CAP.

(d) Based on the intermediate products identified by LC-MS, a possible
degradation pathway including radical reaction, ring open and mineralization was proposed.

Acknowledgments

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References


Figure Captions:

Fig. 1 (A) potential of anode and cathode during MEC acclimation period, (B) CAP concentration change with different cathode electrodes under different conditions, (C) cathode potential with different cathode electrodes during CAP degradation; (D) average circuit current density in MEC with different metal electrodes (Electrolyte conductivity = 5.3 mv S\(^{-1}\), initial pH = 6.0, initial CAP concentration = 32 mg L\(^{-1}\), reaction time = 120 h, applied voltage = 0.3 V)

Fig. 2 (A) CAP concentration during the degradation with three electrodes, (B) circuit current density of three electrodes for CAP degradation, (C) cathode potential in MEC as a function of operation time (Electrolyte conductivity = 5.3 mv S\(^{-1}\), initial pH = 6.0, initial CAP concentration = 32 mg L\(^{-1}\), reaction time = 120 h, applied voltage = 0.5 V)

Fig. 3 Cyclic voltammetry tests carried out on the various cathodes with the (A) presence or absence of oxygen in the catholyte with 32 mg L\(^{-1}\) CAP (B) presence or absence of oxygen in the catholyte without CAP (C) Cyclic voltammetry of copper foam electrode in 32 mg L\(^{-1}\) CAP solution at different scan rates (D) peak current vs. the square root of scan rate

Fig. 4 (A) Nyquist plots of EIS spectra by different electrodes in 32 mg L\(^{-1}\) CAP solution. (B) Component analysis of internal resistance for different material cathodes (fit with the equivalent circuit)
Fig. 5 The LC–MS profiles of the CAP degradation products by (A, B, C) Cu and CR electrodes, (D) NF under 0.3 V applied voltage

Fig. 6 The LC–MS profiles of the CAP degradation products under 0.5 V

Fig. 7 Possible pathways for CAP degradation

Table 1 The efficiency for the CAP degradation with different cathode materials (operation time: 120 h)
Fig. 1 (A) potential of anode and cathode during MEC acclimation period, (B) CAP concentration change with different cathode electrodes under different conditions, (C) cathode potential with different cathode electrodes during CAP degradation; (D) average circuit current density in MEC with different metal electrodes (Electrolyte conductivity = 5.3 mS S⁻¹, initial pH = 6.0, initial CAP concentration = 32 mg L⁻¹, reaction time = 120 h, applied voltage = 0.3 V)
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<th>Parameters</th>
<th>CAP removal</th>
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<td>NF 94.88</td>
<td>0.022 0.95 31.94</td>
<td>26.59 0.06</td>
</tr>
</tbody>
</table>

Noted : AP: applied voltage