Accelerating Electricity Generation and Cr (VI) Removal Using Anatase–Biochar-Modified Cathode Microbial Fuel Cells

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Abstract: Microbial fuel cells (MFC) have considerable potential in the field of energy production and pollutant treatment. However, a low power generation performance remains a significant bottleneck for MFCs. Biochar and anatase are anticipated to emerge as novel cathode catalytic materials due to their distinctive physicochemical properties and functional group architectures. In this study, biochar was utilized as a support for an anatase cathode to investigate the enhancement of the MFC power generation performance and its environmental impact. The results of the SEM and XPS experiments showed that the biochar-supported anatase composites were successfully prepared. Using the new cathode catalyst, the maximum current density and power density of the MFC reached 164 mA/m² and 10.34 W/m², respectively, which increased by 133% and 265% compared to a graphite cathode (70.51 mA/m² and 2.83 W/m²). The degradation efficiency of Cr (VI) was 3.1 times higher in the biochar-supported anatase MFC than in the graphite cathode. The concentration and pH gradient experiments revealed that the degradation efficiency of Cr (VI) was 97.05% at an initial concentration of 10 mg/L, whereas a pH value of two resulted in a degradation efficiency of 94.27%. The biochar-supported anatase composites avoided anatase agglomeration and provided more active sites, thus accelerating the cathode electron transfer. In this study, natural anatase and biochar were ingeniously combined to fabricate a green and efficient electrode catalyst, offering a novel approach for the preparation of high-performance positive catalysts as well as a sustainable, economical, and environmentally friendly method for Cr (VI) removal in aqueous solutions.

Keywords: cathode catalysis; MFC; biochar; anatase; Cr (VI) pollution

1. Introduction

Environmental pollution and energy shortages are common challenges facing the world [1,2]. Notably, pollutants are mainly divided into organic pollutants and heavy metals [3]. In recent years, with the development of industrialization, heavy metal pollution has been inevitable in electroplating, textiles, and other fields [4,5]. Chromium (Cr (VI)), as a mordant or impregnant, is one of the most commonly used heavy metals, which can be severely harmful to human health [6]. It can be difficult to degrade Cr (VI) persistently using traditional methods, such as physical and chemical methods, which commonly exhibit disadvantages of secondary contamination [7]. Therefore, it is imperative to explore eco-friendly and sustainable approaches for the removal of Cr (VI) heavy metals.

Microbial fuel cells (MFCs) are specialized devices that employ electroactive microorganisms to convert organic compounds into electrical energy. [8]. As a novel type of
bioelectrochemical system, MFCs exhibit significant potential for the degradation of heavy metal pollution [9–11]. However, low power generation efficiency has been a bottleneck in the development of MFCs, which is primarily caused by energy loss during activation and concentration/mass transport and ohms loss during MFC operations [12]. Therefore, the practical application of microbial fuel cells in pollutant degradation has not been extensively explored [13,14]. Therefore, researchers have been searching for suitable approaches to improve the performance of MFCs [15,16]. Among several improvement methods, using highly efficient electrode catalytic materials has always been a research hotspot [17–19]. Chen et al. immobilized CNT/ NiCoAl-LDH onto a stainless steel mesh substrate to serve as the cathode in the MFC. The voltage reached 450 mV, and the maximum power density was $433.5 \pm 14.8$ mW/m$^2$ [20]. It should be noted that the physical and chemical properties of cathode materials, such as the conductivity, surface roughness, ductility, and biocompatibility, have a direct impact on the efficiency of electricity generation in batteries [21]. Platinum (Pt) is widely used in cathode catalysts due to its high catalytic performance, which greatly improves the power generation performance of MFCs [22]. In ethanol fuel cells, the Pt/Ru–Sn oxide/C catalyst effectively enhances the current and power density of the cell [23]. Furthermore, for the thermal decomposition of Ru–Sn mixed oxide and the adsorption of Pt nanoparticles, an anode catalyst with strong low potential activity was prepared and its battery voltage was between 0.3 V–0.5 V [24]. However, high costs limited its industrial application. In recent years, the synthesis of non-noble metal electrode catalysts has garnered significant attention from researchers. Lu et al. [25] developed a porous nitrogen doped carbon material and encapsulated iron-based nanoparticles (Fe-Nx/C) as the MFC cathode catalysts, which has a higher catalytic performance than that of the Pt catalysts and a maximum power density of 1227 mW/m$^2$. Despite its excellent performance, the catalyst’s complex manufacturing process poses new challenges for large-scale implementation. Therefore, it is imperative to identify and develop more environmentally friendly and easily available cathode catalytic materials.

Compared to synthetic materials, natural minerals are more environmentally friendly and widely distributed on Earth. It is noteworthy that the utilization of natural minerals as cathode catalysts to enhance the microbial fuel cell performance has received significant attention. Ren et al. [26] used natural hematite as the cathode catalyst to increase the maximum power density of the MFC by 2.2 times compared to the blank group. It is worth noting that TiO$_2$, as a typical semiconductor mineral, has considerable application potential as a cathode catalyst [27]. TiO$_2$ itself exhibits electrochemical properties that can enhance the catalytic activity of oxygen reduction reactions, and it can also transport electrons [28]. Based on the above features of TiO$_2$, researchers have developed a one-dimensional TiO$_2$/Fe$_2$O$_3$ photoanode that can effectively improve the MFC power generation performance [29]. Furthermore, when TiO$_2$ was used as cathode catalyst in microbial electrosynthesis, the yield of acetic acid was increased by 2.14 times [30]. Moreover, Zhang et al. [31] developed a new MFC device, which used manganese dioxide/titanium dioxide/graphite carbon nitride-coated granular-activated carbon as the cathode, and realized the efficient treatment of industrial wastewater with high concentrations of organic acids. However, the agglomeration of TiO$_2$ particles has a certain impact on further enhancing the performance of MFCs. Biochar is an environmentally friendly, low-cost porous material rich in various functional groups that has a high specific surface area and voidage and is often used as a carrier. Notably, it exhibits corrosion resistance, a low ohmic resistance, and high conductivity [32]. Therefore, biochar is widely employed as a supporting material for electrode catalysts [33,34]. Sludge biochar was utilized as a cathode catalytic material by Yuan et al. [35]. The MFC equipped with the sludge biochar had a high redox peak current and obtained a maximum power density of $500 \pm 17$ mW/m$^2$. Therefore, it is necessary to combine the biochar with TiO$_2$ to explore its influence on the performance of MFCs. It should be noted that relatively little research has been conducted on the combination of natural minerals and biochar as catalysts for MFC electrodes.
In our study, we developed a novel biochar-supported anatase (Ana-B) electrode catalyst and integrated it into the cathode of an MFC. The effect of the new electrode catalyst on the performances and electrochemical properties of the MFC were discussed as well as the effect of the catholyte conditions on the Cr (VI) removal. Additionally, the catalytic mechanism of the novel catalyst and its impact on enhancing the power generation performance in MFCs were investigated. Based on the research findings, we are confident that biocarbon-supported anatase can effectively mitigate anatase agglomeration and broaden the pool of MFC cathode catalysts. The cost-effectiveness and efficiency of this positive catalyst have labeled it as a highly promising tool for improving both the MFC power generation performance and pollutant treatment.

2. Materials and Methods

2.1. Chemicals for the Experiment

Anatase was collected from the Lingshou mining area, Hebei Province, China. Polytetrafluoroethylene ((C\(_{2}\)F\(_{4}\))\(_{n}\)), ethanol (C\(_{2}\)H\(_{6}\)O), tryptophan (C\(_{11}\)H\(_{12}\)N\(_{2}\)O\(_{2}\)), sodium chloride (NaCl), potassium chloride (KCl), yeast extract fermentation (YEF), and casein tryptone were purchased from the Tianjin Damao Chemical Reagent Factory. In addition, the chemicals used in the experiments were all analytically pure, and the water used was deionized.

2.2. Preparation of Maize Biochar and Ana-B

Corn cobs sourced from Gansu, China were selected and sun-dried for five days before being ground into powder. The powder was placed in an N\(_{2}\) atmosphere and an oxygen-free environment was created using N\(_{2}\), with a N\(_{2}\) inlet flow rate of 0.5 L/min. The biochar was obtained through a two-hour heating process in a muffle furnace, with the preparation conditions set at a heating rate of 5\(^{\circ}\)C/min and a temperature of 350\(^{\circ}\)C. The prepared biochar was sent through a 200-mesh sieve in dry glassware for later use.

The biochar–anatase composite was synthesized via oxygen-limited pyrolysis of biochar and 75\% (mass ratio) anatase at 500\(^{\circ}\)C under the aforementioned biochar preparation conditions. The prepared compound was repeatedly ground and passed through a 200-mesh sieve, then placed in dry glassware for standby (mark as Ana-B).

2.3. Characterization of Composites

Using an X-ray photoelectron spectroscopy (XPS, UltimaIV, Rigaku, Japan) analysis, the element type characteristics of the original biochar and Ana-B were compared and analyzed. The determination of the valence state and functional group types of element C in the material itself facilitated the elucidation of the mechanism underlying the heavy metal adsorption using the modified biochar materials in the subsequent experiments. Scanning electron microscopy (SEM, JSM-6510, Rigaku, Japan) is commonly used to describe the basic microstructure of materials. The micro-morphologies of the biochar and Ana-B were observed using SEM operated at 10 kV, and the working distance was 10 mm. The structures and compositions of the anatase, biochar, and the Ana-B composites were characterized via X-ray diffraction (XRD) using an Ultima IV X-ray diffractometer (Rigaku Corporation, Rigaku, Japan) with a scanning range from 10 to 80\(^{\circ}\) at a rate of 4\(^{\circ}\) min\(^{-1}\).

2.4. Construction and Operation of the MFC

The experimental apparatus was based on a conventional two-compartment MFC (liquid volume of 60 mL per chamber). The two chambers were separated by an ion-exchange membrane of appropriate dimensions. Graphite plates of the same size (3.5 cm \(\times\) 6 cm) were used as the anode, and each anode chamber was sealed with rubber diaphragms (Figure 1). To investigate the catalytic activity of anatase attached to the biochar, we established the four MFCs as mentioned above. The ordinary graphite electrode, natural anatase-coated electrode, corn biological carbon-coated electrode, and corn biological carbon-loaded anatase-coated electrode were used as the cathodes for each MFC. The control group consisted of ordinary graphite electrodes, while the other three experimental
groups were prepared using a two-step process. Specifically, 0.3 mL of polytetrafluoroethylene and a few drops of ethanol were added to 0.3 g each of anatase, corn biocarbon, and Ana-B. The mixture was stirred until it solidified into gel. The gel was applied to the graphite electrode (Hong feng Carbon, Shanghai, China) (area 3.5 × 6 cm², thickness 5 mm) to form a thin mineral film with a thickness of approx. 0.2 mm, which was air-dried at room temperature for 12 h. The four groups of MFCs were, respectively, placed in a 35 °C incubator.

![Schematic diagram of the MFC device.](image)

An open cathode chamber with a 1.7 mm diameter was reserved on each cathode chamber to ensure good contact with air. Each anode cavity was filled with 10 g/L of tryptophan, 5 g/L of yeast paste, and 10 g/L of NaCl of Luria-B retain (LB). Subsequently, 1 g of soil containing a microbial community collected from Lan Zhou University in Gansu Province was introduced into the anode chamber, while a 0.1 M KCl solution served as the cathode electrolyte. In each MFC, titanium wire was used to connect the circuit. The outer circuit was connected to a 1000 Ω resistor for the electron transfer, which allowed us to measure the voltage of the outer circuit.

2.5. Measurement and Analysis of the Pollutant Degradation Performance

After four types of MFCs with different cathodes were configured to reach a stable state, a 20 mg/L Cr (VI) solution was used to replace the cathode solution. A specific volume of liquid was extracted from the cathode chamber on an hourly basis and its concentration was analyzed. The UV visible spectrophotometer used the standard curve method to determine the concentration of Cr (VI) and the degradation efficiency. Based on the standard curve correlating the chromium concentration with absorbance, the concentration of Cr (VI) in the sample was determined. Concentration gradients ranging from 10 to 70 mg/L and pH gradients spanning a range from two to five were utilized. The above experiment was repeated under other conditions to explore the impact of these conditions on the degradation performance of the MFC.
3. Results

3.1. Characteristics of Ana-B

As observed from the SEM images (Figure 2a,b), the primitive biochar presented a compact and highly ordered fibrous or sheet-like structure with a small number of pore structures of different sizes. However, after anatase was compounded, the biochar crystal deformation was small and more broken (Figure 2c,d). The mean particle size of the biochar was approximately 40–50 µm, whereas that of Ana-B was approx. 30 µm. Moreover, the Ana-B exhibited fragmentation and its surface was rough (Figure 2c,d), whereas the surface of the biochar was very smooth (Figure 2a,b). At the same time, anatase was evenly distributed around the biochar. The alterations in the microscopic morphological characteristics of the biochar suggested a successful compounding between anatase and the biochar.

![Figure 2. The SEM images of biochar (a,b) and Ana-B (c,d).](image-url)

The biochar and Ana-B composites underwent an XRD analysis, as shown in Figure 3. The resulting XRD patterns indicated that the biochar displayed three broad and diffuse amorphous diffraction peaks. Additionally, sharper small diffraction peaks were observed, indicating the carbonization of the biochar. This led to the formation of microcrystalline carbon with a more refined grain structure that was graphitized. It was noteworthy that Ana-B exhibited anatase diffraction peaks at 2θ angles of 29.2°, 36.1°, 41°, 4°, 48.5°, 54.4°, and 61.0° which corresponded to the (101), (004), (101), (200), (211), (204), and (215) crystal faces of anatase, respectively. These results demonstrated the successful preparation of the composite material with a relatively stable biochar–anatase structure.

For the above conclusion, the X-ray photoelectron spectroscopy (XPS) patterns for the biochar and Ana-B (Figure 4) provided further evidence. The full spectrum scanning diagram of the biochar before and after loading anatase is presented in Figure 2. It can be seen from the figure that the characteristic binding energy peaks of O1s and C1s appeared before and after the adsorption, and the characteristic binding energy peak of Ti2p appeared after loading anatase. The binding energy of the O1s and C1s characteristic peaks was approx. 529 eV and 280 eV (Figure 4a). The binding energy of the Ti2p characteristic peak was approx. 454 eV (Figure 4b). After loading anatase, the intensity of the O1s diffraction peak increased, while the intensity of the C1s diffraction peak decreased (Figure 4b). Figure 4 proves that anatase was successfully loaded onto the biochar. This further confirmed that
anatase alters both the elemental composition and content, as well as the microscopic morphology of biochar.

Figure 3. XRD patterns of biochar and Ana-B.

Figure 4. The XPS images of biochar (a) and Ana-B (b).

3.2. Electricity Generation Performance of the MFC

The utilized electrode material plays a crucial role in determining the current density and energy conversion efficiency of MFCs. Several studies have shown that the material composition and physical properties of the cathode can produce significant enhancements that affect the current density and energy conversion efficiency of MFCs [36]. An analysis of the electricity generation performance of the four MFCs is presented in Figure 5a. The polarization and power density curves were comparatively examined to provide a visual representation of the MFC performance. The limiting voltage with the Ana-B MFC reached 311.34 mV (Table 1), which was 26.54% and 54.51% higher than the anatase MFC (246.00 mV) and biochar MFC (201.47 mV), respectively. Furthermore, the limiting current densities for Ana-B, anatase, and biochar were 164.00 mA/m², 124.81 mA/m², and 102.52 mA/m², respectively, which were 132.6%, 77.0%, and 45.4% higher than the blank, respectively. Notably, the maximum power density of the MFC system was achieved when the external resistance approached its internal resistance, highlighting the importance of optimizing these parameters for efficient energy generation. Ana-B, anatase, and biochar all had maximum power densities of 10.34 mW/m², 7.22 mW/m², and 5.94 mW/m², respectively, while the blank had only 2.84 mW/m². Of these four MFCs, the Ana-B MFC had the highest electrogenesis capacity. This outcome was originally ascribed to the biochar-supported anatase composites that possessed abundant functional groups on their surface, thereby exhibiting an excellent electron transport capability [37,38].
1.10 mW/m², the initial anode potential of the Ana-B-based MFC device increased by 89.03% (Figure 5b) compared to the previous studies, suggesting that this high-efficiency MFC could likely be utilized in MFC devices that utilized organic matter electrodes, such as a white oak charcoal-based cathode.

Furthermore, the polarisation curve of the Ana-B MFC was significantly improved compared to previous studies. The maximum power density of the Ana-B-based MFC was observed to be 2.90 mW/m², which was higher than that of this device. Additionally, the slope of the Ana-B MFC anode potential curve was much lower than that of the other systems, indicating that the anode maintained a lower potential for a long time. This system exhibited a reduced polarization and an

The presented polarization curves revealed that the electrode performance of Ana-B, anatase, and biochar were higher than the blank, demonstrating that the application of Ana-B was beneficial for increasing the output power and current of the MFC and reducing the internal resistance of the MFC. Moreover, the power generation efficiency of the Ana-B-based MFC was significantly improved compared to previous studies. The maximum power density of the Ana-B-based MFC device increased by 89.03% (Figure 5b) compared to a power density of 5.47 mW/m² for the Fe-Mn-Mg/CF composite cathode [36]. Regarding the output power, the Ana-B-based MFC was significantly enhanced compared to an Fe-anode and bio-cathode-based MFC device (maximum power density of approximately 1.10 mW/m²) [39]. The Ana-B-based MFC had an 840% higher maximum power density than this device.

Additionally, the Ana-B MFC exhibited an enhanced output power compared to other MFC devices that utilized organic matter electrodes, such as a white oak charcoal-based MFC device with a maximum power density of 2.90 mW/m². This comparative study showed a significant improvement in the power generation efficiency of the Ana-B MFC compared to the previous studies, suggesting that this high-efficiency MFC could likely have a higher pollutant removal performance. Notably, the oxygen reduction reaction processed at the MFC cathode exhibited sluggish kinetics, and efficient electrode catalysts served to expedite this process, thereby enhancing the battery performance [40]. Furthermore, the combination of biochar and TiO₂ effectively solved the easy recombination of holes and electrons, thereby improving the electrical production performance of the MFC [41].

In order to further investigate the impact of Ana-B on the MFC electrode potential, an electrode potential curve was measured, as illustrated in Figure 6. The initial anode potential varied significantly among the different systems. The initial anode potential of the Ana-B MFC was observed to be -335 mV (Figure 6), which was comparatively lower than that of the other systems. In addition, the slope of the Ana-B MFC anode potential curve was much lower than that of the other systems, indicating that the anode maintained a lower potential for a long time. This system exhibited a reduced polarization and an

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**Table 1.** Polarization curve and power density curve parameters.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Open Circuit Voltage (mV)</th>
<th>Maximum Power Density (mW/m²)</th>
<th>Limiting Current Density (mA/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ana-B</td>
<td>311.34</td>
<td>10.34</td>
<td>164.00</td>
</tr>
<tr>
<td>Anatase</td>
<td>246.00</td>
<td>7.22</td>
<td>124.81</td>
</tr>
<tr>
<td>Biochar</td>
<td>201.47</td>
<td>5.94</td>
<td>102.52</td>
</tr>
<tr>
<td>Blank</td>
<td>160</td>
<td>2.83</td>
<td>70.57</td>
</tr>
</tbody>
</table>

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**Figure 5.** Polarization curves (a) and power density curves (b) of the MFC equipped with different cathode catalysts.
enhanced electron transmission capacity. For the cathode, the initial cathode potential of the Ana-B MFC was the highest at $-27.5$ mV (Figure 6b). The cathode potential curve displayed a significantly lower degree of polarization and a superior electron receiving capacity compared to the other systems, indicating a favorable electrochemical performance. Therefore, the Ana-B cathode catalyst effectively enhanced the anode and cathode electrode potential difference, making the redox reaction easier. At the same time, it also showed that Ana-B increased the electron transfer rate of the cathode.

![Figure 6. Anode potential (a) and cathode potential curves (b) of the MFC equipped with different cathode catalysts.](image)

3.3. Study on the Cr (VI) Degradation Performance of the MFC

Furthermore, a positive correlation existed between the electricity generation efficiency and the pollutant removal efficiency [11], indicating the potential environmental impact of the efficient electrode materials. The enhancement of the electricity generation efficiency was taken into consideration, and the Ana-B-based MFC was likely to exhibit a higher efficiency for wastewater treatment. Especially for Cr (VI) pollution, Cr (VI) was reduced to Cr (III) using MFC bioelectrons, thus reducing the migration and toxicity of Cr (VI) [42]. The degradation rates for Cr (VI) in different MFCs are shown in Figure 7. At the same time, the Ana-B, anatase, and biochar MFCs exhibited degradation rates of 94.0%, 68.2%, and 41.9%, respectively, while the blank MFC only had a rate of 22.5% (Figure 7a). There was no doubt that the degradation rate of Ana-B-based MFC reached a maximum value of 94.0%. Based on the computational results, Ana-B, anatase, and biochar exhibited degradation rate improvements of 71.5%, 45.7%, and 19.4%, respectively, compared to the blank MFC. Notably, compared to the previous studies, the degradation rate of Cr (VI) increased by 11.85% [43]. In addition, Cr (VI) acted as an electron acceptor in the cathode. The higher the electron transfer efficiency of the MFC system, the faster the removal rate of Cr (VI) [11].

The kinetic study of the adsorption process was mainly used to describe the adsorption rate of hexavalent chromium by the adsorbent, and the data was fitted by the kinetic model to discuss the adsorption mechanisms. The corresponding degradation kinetic curves are presented in Figure 5b, where $C_0$ represents the initial concentration of Cr (VI) in the aqueous solution and $C$ denotes the actual concentration of Cr (VI) at a specified reaction time. Additionally, $k$ signifies the rate constant for the degradation. The degradation rate constants $k$ for Cr (VI) in the different MFCs are shown in Table 2. The Ana-B MFC had the highest reaction rate constant $0.3318 \pm 0.0116$, which further indicated that the system had the fastest Cr (VI) degradation rate. This could be attributed to the fact that a higher rate constant indicated a higher probability of Cr (VI) molecules colliding with the active sites of the catalyst, leading to a faster conversion [44].
Figure 7. Cr (VI) degradation curves (a) and kinetic fitting curves (b) were equipped with the MFC of different cathode catalysts.

Table 2. Reaction dynamics fitting parameters of the system for Cr (VI) degradation.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Fitting Equation</th>
<th>Reaction Rate Constant (K/d⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ana-B</td>
<td>y = Intercept + Slope * x</td>
<td>0.3318 ± 0.0116</td>
<td>0.9915</td>
</tr>
<tr>
<td>Anatas</td>
<td>y = Intercept + Slope * x</td>
<td>0.145 ± 0.0054</td>
<td>0.99</td>
</tr>
<tr>
<td>Biochar</td>
<td>y = Intercept + Slope * x</td>
<td>0.0631 ± 0.0028</td>
<td>0.9871</td>
</tr>
<tr>
<td>Blank</td>
<td>y = Intercept + Slope * x</td>
<td>0.0306 ± 0.0008</td>
<td>0.9951</td>
</tr>
</tbody>
</table>

3.4. Effect of the Solution Initial Concentration

According to prior research, when diverse microbial fuel cells are employed for the treatment of pollutants in wastewater, the degradation efficiency of the pollutants will be affected by multiple external factors, among which the initial concentration of pollutants is a relatively important factor [11]. Therefore, we further investigated the impact of varying pollutant concentrations on the degradation efficiency. This factor is universal in the degradation of different types of pollutants and can affect the degradation efficiency of Cr (VI) pollutants using MFCs. This study examined the influence of varying concentrations of Cr (VI) on the MFC performance. Four different initial concentrations (10 mg/L, 30 mg/L, 50 mg/L, and 70 mg/L) were used to investigate the degradation rate of MFCs in response to different pollution levels.

The degradation curves of Cr (VI) under different concentration conditions are shown in Figure 8a. The negative logarithm of the ratio of the residual concentration to the initial concentration was proportional to time. With the change of time, the existing concentration decreased continuously, which indicated that the MFC could degrade Cr (VI) at different Cr (VI) concentrations. The degradation efficiency of Cr (VI) decreased as the initial concentration of Cr (VI) increased. After 9 h, the degradation efficiency of the four concentrations from small to large were 97.05% (10 mg/L), 87.43% (30 mg/L), 55.25% (50 mg/L), and 37.34% (70 mg/L), respectively. When the initial concentration of Cr (VI) was 10 mg/L, the degradation efficiency of the four initial concentration groups was the highest, which reached 97.05% for the entire group. When the concentration of Cr (VI) reached 70 mg/L, the degradation efficiency for all four initial concentration groups was only 37.34%. With the increase in the concentration, the degradation efficiency decreased significantly. Due to the absence of degradation substrates in the subsequent reaction, the treatment rate of Cr (VI) was lower than that observed at a concentration of 30 mg/L after 9 h. When exploring the degradation of Cr (VI) using MFCs at the initial concentration of solution, if was found that the lower the concentration, the higher the degradation efficiency. This finding was in line with prior research outcomes [45]. The main reason for this phenomenon was that when the concentration of Cr (VI) was high, the electron acceptor in the cathode chamber received an excess of electrons compared to those produced by
metabolic activities on the anode side, resulting in a reduction in the Cr (VI) degradation rate [46]. The increase in the initial concentration of Cr (VI) could be due to the increase in the number of electronic AC receptors and the decrease in the electrochemical activity of Cr (VI) [47].

![Figure 8](image_url)

Figure 8. Effect curve (a) and kinetic fitting curve (b) of the initial concentration on the degradation of Cr (VI) using the Ana-B MFC.

In order to reveal the kinetics of the degradation for the lower Ana-B MFC at different Cr (VI) concentrations, the kinetics of the Cr (VI) degradation time curve was fitted (Figure 8b). The findings indicated that the degradation process followed a complex first-order kinetics model. The fitting index value represented a good fit (R² > 0.99) (Table 3). It was noteworthy that the Ana-B MFC system at a concentration of 10 mg/L achieved a maximum reaction rate constant of 0.3832 ± 0.0187 d⁻¹. Therefore, the degradation rate of the Ana-B MFC system with an initial concentration of 10 mg/L was the fastest.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Fitting Equation</th>
<th>Reaction Rate Constant (K/d⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ana-B</td>
<td>y = Intercept + Slope * x</td>
<td>0.3832 ± 0.0187</td>
<td>0.98125</td>
</tr>
<tr>
<td>Anatase</td>
<td>y = Intercept + Slope * x</td>
<td>0.2113 ± 0.0055</td>
<td>0.9945</td>
</tr>
<tr>
<td>Biochar</td>
<td>y = Intercept + Slope * x</td>
<td>0.0847 ± 0.0027</td>
<td>0.9915</td>
</tr>
<tr>
<td>Blank</td>
<td>y = Intercept + Slope * x</td>
<td>0.0518 ± 0.0039</td>
<td>0.9548</td>
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</table>

3.5. Effect of Solution pH

According to the previous studies, the pH is one of the fundamental factors in the electrochemical reaction [48]. This factor is prevalent in the reactions of various types of microbial fuel cells for pollutant degradation, and this study further examined the impact of different pH values on the Cr (VI) degradation efficiency in MFCs. The effect of the pH on the efficiency of Cr (VI) degradation using the Ana-B MFC is shown in Figure 9. In this experiment, four different initial pH values (ranging from two to five) were tested in order to investigate the impact of varying pH levels on the MFC performance. The starting concentration of the pollutant was 20 mg/L. As the reaction time increased, there was a continuous decrease in the C/C₀ value of Cr (VI), indicating that the Ana-B MFC had the ability to degrade various concentrations of Cr (VI). As shown in Figure 9a, the degradation efficiency of the four concentrations from small to large were 94.275% (pH = 2), 87.850% (pH = 3), 65.725% (pH = 4), and 48.525% (pH = 5) after 9 h, respectively. The degradation efficiency of Cr (VI) was pH-dependent, with the highest efficiency observed at a pH of two in the reaction system. Over time, the degradation rate of the pollutants gradually decreased in each unit of time, as evidenced by the gradual decrease in the slope of each interval, which was typical for the experimental group with a pH value of two. This result
was also consistent with the optimal pH for Cr (VI) degradation close to 2, which was consistent with the previous studies [45]. Additionally, the solution’s acidity impacted the adsorbent’s surface charge, resulting in a positively charged electrode catalyst surface in the Cr (VI) solutions under acidic conditions. This was conducive to improving the electron transfer efficiency of the system, which accelerated the degradation of Cr (VI) [29].

![Figure 9](a) and kinetic fitting curve (b) of the pH on the degradation of Cr (VI) using the Ana-B MFC.

The degradation kinetics of Cr (VI) were further investigated by fitting the time curve under varying pH conditions. The results indicated that the degradation process of Cr (VI) followed first-order kinetics (Figure 9b). The fitting index values indicated a good fit ($R^2 > 0.98$) (Table 4). Among them, when pH = 2, the kinetic constant of the Ana-B MFC was the highest (0.3107 $\pm$ 0.00385 k$^{-1}$). Therefore, at a pH of 2, the degradation rate of Cr (VI) in the Ana-B MFC system was maximized.

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<thead>
<tr>
<th>Systems</th>
<th>Fitting Equation</th>
<th>Reaction Rate Constant (K/d$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ana-B</td>
<td>$y = \text{Intercept} + \text{Slope} \times x$</td>
<td>0.3107 $\pm$ 0.00385</td>
<td>0.9863</td>
</tr>
<tr>
<td>Anatase</td>
<td>$y = \text{Intercept} + \text{Slope} \times x$</td>
<td>0.2392 $\pm$ 0.0105</td>
<td>0.9847</td>
</tr>
<tr>
<td>Biochar</td>
<td>$y = \text{Intercept} + \text{Slope} \times x$</td>
<td>0.1235 $\pm$ 0.0059</td>
<td>0.9818</td>
</tr>
<tr>
<td>Blank</td>
<td>$y = \text{Intercept} + \text{Slope} \times x$</td>
<td>0.0777 $\pm$ 0.0022</td>
<td>0.9935</td>
</tr>
</tbody>
</table>

3.6. Mechanism of the Ana-B Cathode Catalysis

In this study, biochar-supported anatase was used as the MFC cathode catalyst to effectively improve its power generation performance (Figure 10). TiO$_2$ is a kind of semiconductor mineral with a band gap of about 3.0–3.2 eV [27]. The Ti (IV) site located on the surface of the TiO$_2$ crystal sequestered conduction electrons, leading to its reduction to a Ti (III) site. The oxygen (O$_2^-$) molecules adsorbed on the cathode surface of the MFC reacted with the Ti (III) center to form the superoxide-free radical (O$_2^-$), which enhanced the oxygen reduction reaction in the cathode center and promoted the power generation of the MFC [49]. In addition, compared to the other metal oxide semiconducting materials, anatase had a higher Ti–O bond polarity, and water molecules adsorbed on the surface were easy to be polarized and dissociated to form a hydroxyl group [50,51]. In a liquid medium, the presence of surface hydroxyl groups enhanced the performance of TiO$_2$ by facilitating the adsorption of charged molecules through electrostatic interactions. This resulted in the formation of a diffuse electric double layer that increased the electron retention capacity [52].
Biochar loaded anatase avoided anatase agglomeration and effectively improved the catalytic performance of the cathode. Meanwhile, the biochar possessed a graphite-like structure and redox-active quinoline groups, which endowed it with numerous active sites and unsaturated electron pairs [53]. This enabled the biochar to accelerate the electron transfer and pollutant reduction transformation, thus improving the MFC cathode reaction rate and the pollutant removal efficiency [54]. Additionally, the biochar was produced at high temperatures, resulting in a significant concentration of pyrrolic, graphitic, and pyridinic nitrogen that could be utilized as a cathode catalyst to expedite the electron transfer [55].

4. Conclusions

As an efficient and eco-friendly cathode catalyst, Ana-B significantly enhanced the power generation performance of the MFC. The maximum current density of the MFC equipped with an Ana-B cathode was 164 mA/m², and the maximum power density was 10.34 W/m², which were 2.3 and 3.6 times higher than the graphite electrode, respectively. Simultaneously, the MFC equipped with an Ana-B cathode demonstrated a remarkable efficiency in the degradation of Cr (VI) pollution. When the initial concentration of Cr (VI) was 20 mg/L, the removal rate of Ana-B MFC was close to 94% after 8 h, while that of blank control group was only 22.5%. The experimental results indicated that a lower initial concentration of Cr (VI) led to a higher removal efficiency across different gradients. When the initial concentration was 10 mg/L, the highest removal rate of the Ana-B MFC was 97.05%. Additionally, at a pH of two, the Ana-B MFC system exhibited a maximum removal rate of 94.27% for Cr (VI), indicating a superior removal efficiency. It is worth noting that Ana-B, as a cathode catalyst, enhanced the redox process of the cathode and accelerated the electron transfer of the cathode, thus effectively improving the electrical performance of the MFC. Therefore, the low-cost and pollution-free mineral biochar composite served as an effective positive catalytic material, which holds great significance for addressing the issue of low efficiency in MFC power generation. Currently, the low efficiency of high-concentration Cr (VI) degradation remains a bottleneck for Ana-B MFCs. Considering that Ana-B is a photocatalyst, the further use of Ana-B as a photocatalytic material for the cathode will be the target of our next research.
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