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Improved electricity production and nitrogen enrichment during the treatment of black water using manganese ore-modified anodes

Xin Yang¹ · Hongbo Liu¹  · Yangyang Yao¹ · Eric Lichtfouse²

Abstract

The decline of fossil fuel availability is calling for alternative energy such as electricity produced by degradation of waste in microbial fuel cells. The performance of microbial fuel cells is controlled by the anode because microorganisms grow and attach on the anode. Here, we prepared carbon felt electrodes modified with manganese ore based on the hypothesis that manganese and silicon oxides would improve the cell performance to treat simulated black water. We compared properties of the manganese ore-modified electrodes with properties of classical carbon felt electrodes modified with magnetic ferrous oxide. We also studied the removal of the chemical oxygen demand and the enrichment in ammonia nitrogen. Results show that the maximum voltage of the manganese ore-modified carbon felt electrode is 1.7 times higher than that of the magnetic ferrous oxide-modified carbon felt electrode. The start-up time to reach the maximum voltage is reduced by 68%. The removal of chemical oxygen demand reached 91.2%. Up to 68.0% of ammonia nitrogen can be enriched at the cathode, implying that ammonia nitrogen can be highly reduced in the effluent. Overall, the manganese ore-modified carbon felt electrode showed excellent redox performance, excellent corrosion resistance and low electron transfer resistance.

Keywords Black water · Modified electrodes · Ammonium enrichment · Treatment performance · Resource recovery

Introduction

Due to the rapid development of industrialization and urbanization, a large amount of industrial wastewater and domestic sewage is discharged (Panagopoulos et al. 2022; Hasan et al. 2021). This has led to the deterioration of the water environment and caused shortage of water resources (Panagopoulos et al. 2020; Kurwadkar et al. 2022; Panagopoulos et al. 2021). Microbial fuel cells are developed devices that convert the chemical energy stored in organic matter into

electricity by microbial metabolic processes (Tahir et al. 2021). Since treatment of wastewater by microbial fuel cells can both degrade wastewater and produce electricity, microbial fuel cells have attracted attention as a promising green energy source. (Zang et al. 2012). Specifically, the biodegradation of wastewater at the anode generates electrons and protons which are recycled to the cathode to produce electricity (Samsudeen et al. 2015). Therefore, the anode is a key limiting step, whose efficiency controls the overall performance (Fan et al. 2008; Mohamed et al. 2017).

Common anode materials such as graphite, carbon cloth, carbon felt and activated carbon are not efficient enough in terms of energy recovery (Liu et al. 2020; You et al. 2017). Alternatively, anodes made of precious metals such as platinum could improve the degradation of contaminants (Xu et al. 2018), yet such metals are expensive. Therefore, researchers have focused on developing cheaper metals such as magnetic ferric tetroxide, which presents unique physical and chemical properties, small particle size, narrow distribution, stable surface properties, and good biocompatibility (Park et al. 2014; Peng et al. 2012; Li et al. 2008). Manganese ore is attracting attention because the presence of

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manganese oxides improves catalysis and removal of organic matter (Xie et al. 2018). Indeed, MnO_2 is a common redox agent and is often used to decrease the chemical oxygen demand of wastewater (Gao et al. 2018). It is possible to improve corrosion resistance and redox properties of electrodes by modification of the electrodes with the manganese ore since it contains manganese oxides, silicon oxides and other metal oxides (Li et al. 2020).

The performance of electrode materials can be improved by modification with both metal and non-metal materials (Qiao et al. 2007; Zhu et al. 2010; Liu et al. 2014). For instance, due to the lower resistance of charge transfer, modifying a carbon paper anode with iron oxide increased the output power density by 31% (Harshiny et al. 2017). Similarly, a microbial fuel cell carbon felt anode modified with MnO_2 improved the output power to 3580 mW/m^2 , which is 24.7% higher than the unmodified anode (Zhang et al. 2015).

Many researchers focus on the removal of pollutants in water with microbial fuel cells. For example, by using air-cathode microbial fuel cells for wastewater treatment, ammonia nitrogen can be removed up to 99.0% (Yang et al. 2020a, b). Nitrification/denitrification can be enhanced by constructing a multi-anode microbial fuel cell (Huang et al. 2020). The removal of organic matter and nutrients from microbial fuel cells can be enhanced by pre-treatment modifications, such as chemical and thermal treatment of carbon brushes (Shahid et al. 2021). However, under the context of circular economy, ammonia nitrogen as a resource should be recovered as much as possible. In this study, we explored the enrichment and recovery of ammonia nitrogen from black water. By doing this, we used the inexpensive and widely available manganese ore for anode modification and prepared carbon felt anodes modified with various amounts of manganese ore and magnetic ferroferric oxide. Besides the enrichment effects on ammonium nitrogen, we also investigated their performance on treating simulated black water and producing electricity in a wastewater microbial fuel cell.

Experimental

Materials

We constructed a dual-chamber and a single-chamber microbial fuel cell; the sizes and start-up method are shown in Supplementary Text S1. The microbial fuel cell was started using the open-circuit constant potential start-up method that we have previously used (Ren et al. 2022). The main composition of the experimentally simulated black water is 1200–1500 mg/L chemical oxygen demand, 90–120 mg/L ammonia nitrogen ($\text{NH}_4^+\text{-N}$) and 8–15 mg/L phosphate ($\text{PO}_4^{3-}\text{-P}$). Detailed composition of the simulated black

water and composition of trace elements in the stock solution are given in Supplementary Tables S1 and S2, respectively.

Preparation of modified anode materials

Manganese ore tailings were obtained from a manganese ore production site in Guangxi, China, which were crushed and passed through a 200-mesh sieve to obtain the powdered manganese ore. Main constituents of the crushed manganese ore powder were determined using the X-ray diffraction analysis (Fig. S1a). The magnetic ferroferric oxide was produced using the co-precipitation method (Chen et al. 2010). X-ray diffraction analysis of the composition of the produced magnetic ferroferric oxide was assessed (Fig. S1b).

The mixture of manganese ore powder (0.8 g), acetylene black (0.1 g) and polyvinylidene fluoride (0.1 g) was mashed to powder in an agate mortar; 1.0 g of this powder was added to 10 mL of N-methylpyrrolidone in a beaker and stirred magnetically for 4 h to form a slurry. This slurry was poured evenly on a 5×4 cm carbon felt and coated with a film applicator; then, the coated electrode was dried for 10 h in a vacuum oven at 102°C to obtain manganese ore-modified carbon felt electrodes with a loading of 1.0 g. According to the above method, 0.5 g, 1.0 g and 1.5 g loaded manganese ore-modified carbon felt electrodes and magnetic ferroferric oxide-modified carbon felt electrodes were prepared similarly. Detailed preparation processes of the manganese ore-modified carbon felt electrodes and magnetic ferroferric oxide-modified carbon felt electrodes could refer to Supplementary Tables S3.

Analysis methods and data acquisition

Electrochemical analysis

Electrochemical properties of the manganese ore-modified carbon felt electrode and the magnetic ferroferric oxide-modified carbon felt electrode were determined using the electrochemical workstation CHI660E (Shanghai Chenhua). A three-electrode system was used for electrochemical analysis, with a platinum electrode as the counter electrode, the modified anode as the working electrode, the saturated calomel electrode as the reference electrode and a 1 mM potassium ferricyanide solution as the electrolyte.

Measurements and calculations

Chemical oxygen demand was measured with the potassium dichromate method (Dhanjai et al. 2019). Ammonia nitrogen was measured with the spectrophotometric method (Lin et al. 2019) and total phosphorus with the ammonium

molybdate spectrophotometric method (Labry et al. 2013). The voltage was recorded every 1 min using the PicoLog online data collector. This closed loop current was calculated according to Ohm's law, and the microbial fuel cell produces a current density I (mA/m^2) that can be obtained by calculating with the equation $I = U/(RS)$. The power density (mW/m^2) was calculated as $P = IU$, where U is the voltage (mV), R is the resistance (Ω), and S is the surface area of the anode (m^2) (Du et al. 2016).

Results and discussion

Carbon felts modified with different loadings of manganese ore and magnetic ferroferric oxide were used as anodes for microbial fuel cells to explore their performance in treating black water.

Electrochemical characterization

Cyclic voltammetry curves of our manganese ore-modified carbon felt electrodes display redox peaks with higher symmetry than the magnetic ferroferric oxide-modified carbon felt electrodes, and the distance between the redox peaks is smaller (Fig. 1a, b). This indicates that the manganese ore-modified carbon felt electrodes has better reversibility after the redox reaction and excellent catalytic oxidation. This observation implies that the manganese ore-modified carbon felt electrode has lower redox resistance and high reversibility favoring the redox reaction, according to the literature (Qiu et al. 2020).

The curves of the manganese ore-modified carbon felt electrode and the magnetic ferroferric oxide-modified carbon felt electrode are similar in the high-frequency region, showing a rounded semicircle (Fig. 1c, d). However, as shown in Table 1, the minimum polarization resistances are $1.0 \Omega/\text{cm}^2$ for the 0.5 g manganese ore-modified carbon felt electrode, $2.0 \Omega/\text{cm}^2$ for the 1.0 g magnetic ferroferric oxide-modified carbon felt electrode and $2.0 \Omega/\text{cm}^2$ for the carbon felt electrode (the polarization resistance values of the other electrodes are shown in Supplementary Table S4). The lowest polarization resistance of the manganese ore-modified carbon felt electrode is likely due to the fact that the manganese oxide has a lower charge transfer resistance compared with the magnetic ferroferric oxide (Zhang et al. 2016). A lower polarization resistance reduces the transfer resistance of electrons and increases the electron mobility (Fan et al. 2017). This is in agreement with the literature verifying that a small amount of manganese ore can improve the electron transfer rate (Aswin et al. 2008). Another explanation is that manganese oxide is known to favor microbial attachment and improve the electron transfer rate (Zhou et al. 2021; Yang et al. 2020a, b). In addition, for the same mass

of manganese dioxide or iron oxide, the amount of electrons absorbed by manganese is higher than that of iron (Jiménez-Cedillo et al. 2011), which could be one of the reasons for the lower resistance of manganese ore-modified carbon felt electrode. Therefore, the electron transfer resistance of the manganese ore-modified carbon felt electrode is lower. Manganese ore-modified carbon felt electrode rich in manganese dioxide makes the electron absorption transfer easier.

Tafel polarization curves demonstrate that the corrosion voltage is -0.10 V for the 0.5 g manganese ore-modified carbon felt electrode versus -0.18 V for the unmodified carbon felt electrode (Fig. 1e, f). In contrast, negative voltages for magnetic ferroferric oxide-modified carbon felt electrodes are maximizing at -0.22 V . The higher corrosion resistance of manganese ore-modified carbon felt electrodes is explained by the higher resistance of manganese oxides and SiO_2 to corrosion (Anzini et al. 2020). The loading of ferroferric oxide leads to more corrosion of the electrode because the ferroferric oxide is an unstable intermediate that tends to rust when contacting air and water. Therefore, manganese ore carbon felt electrodes have better corrosion resistance.

Overall, we found that the manganese ore-modified carbon felt electrode has better redox performance, lower polarization resistance and higher corrosion resistance than magnetic ferroferric oxide-modified carbon felt and carbon felt electrodes, which is more suitable for practical use.

Performance of the single-chamber wastewater microbial fuel cell

The anode materials were 0.5 g manganese ore-modified carbon felt electrode and 1.5 g magnetic ferroferric oxide-modified carbon felt electrode, respectively. Results show that the manganese ore-modified carbon felt electrode increased power production to a maximum voltage of 215 mV in 1100 min, whereas it took 3500 min for the magnetic ferroferric oxide-modified carbon felt electrode to increase power production to a maximum of 124 mV (Fig. 2a). We calculated the maximum power density of the manganese ore-modified carbon felt electrode ($23.11 \text{ mW}/\text{m}^2$) as 3.0 times higher than that of the magnetic ferroferric oxide-modified carbon felt electrode ($7.68 \text{ mW}/\text{m}^2$). This might be explained by the fact that despite the excellent electrical conductivity of the magnetic ferroferric oxide-modified carbon felt electrode (Song et al. 2016), there is more biofilm formation on this electrode, and in turn its electron transfer is limited. This hypothesis is strengthened by a study showing that the grafting of Fe^{2+} onto a graphite polyester composite electrode leads to higher specific surface area and pore space, more biofilm formation and lower power density than the unmodified electrode (Narayanasamy et al. 2018). On the other hand, a study showed that the electrode performance of iron oxide modified electrode was unstable, and the magnetic

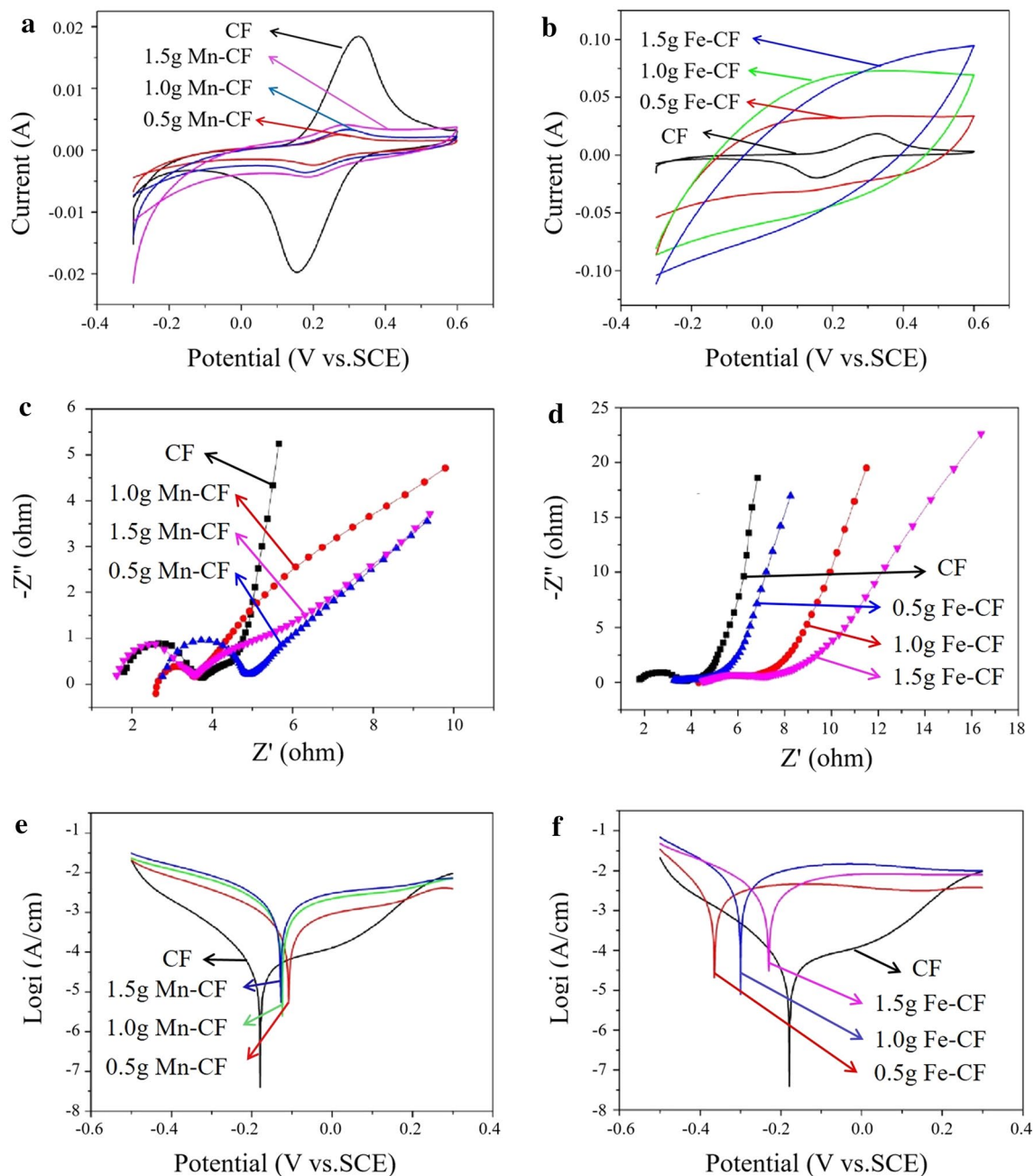


Fig. 1 Comparison of electrochemical characterization of carbon felt (CF), manganese ore-modified carbon felt (Mn-CF) and magnetic ferroferric oxide-modified carbon felt (Fe-CF) electrodes with different loadings: **a, b** cyclic voltammetric curves (reference electrode:

saturated calomel electrode), **c, d** electrochemical impedance spectra curves and **(e, f)** Tafel polarization curves. Note manganese ore-modified carbon felt (Mn-CF) electrode has better redox peak and higher corrosion voltage

ferroferric oxide itself was also an unstable iron intermediate oxide which is easily oxidized to generate iron oxide rust and seriously affects the electron transfer effect (Fu et al. 2014). Moreover, manganese dioxide increases the electrode wettability and the attachment of microorganisms that allows electronic transfer (Gohari et al. 2014). In contrast, the electrode resistance of manganese ore-modified carbon felt electrode is lower, so the manganese ore-modified carbon

felt electrode is easier for electron transfer. And its time to reach the maximum voltage is faster. Overall, we find that the manganese ore-modified carbon felt electrode produces more electricity and has a shorter start-up time and a greater power density.

As shown in Fig. 2b and c, the chemical oxygen demand removal effect of both electrodes is similar. The removal rate reaches 91.2% for the manganese ore-modified carbon

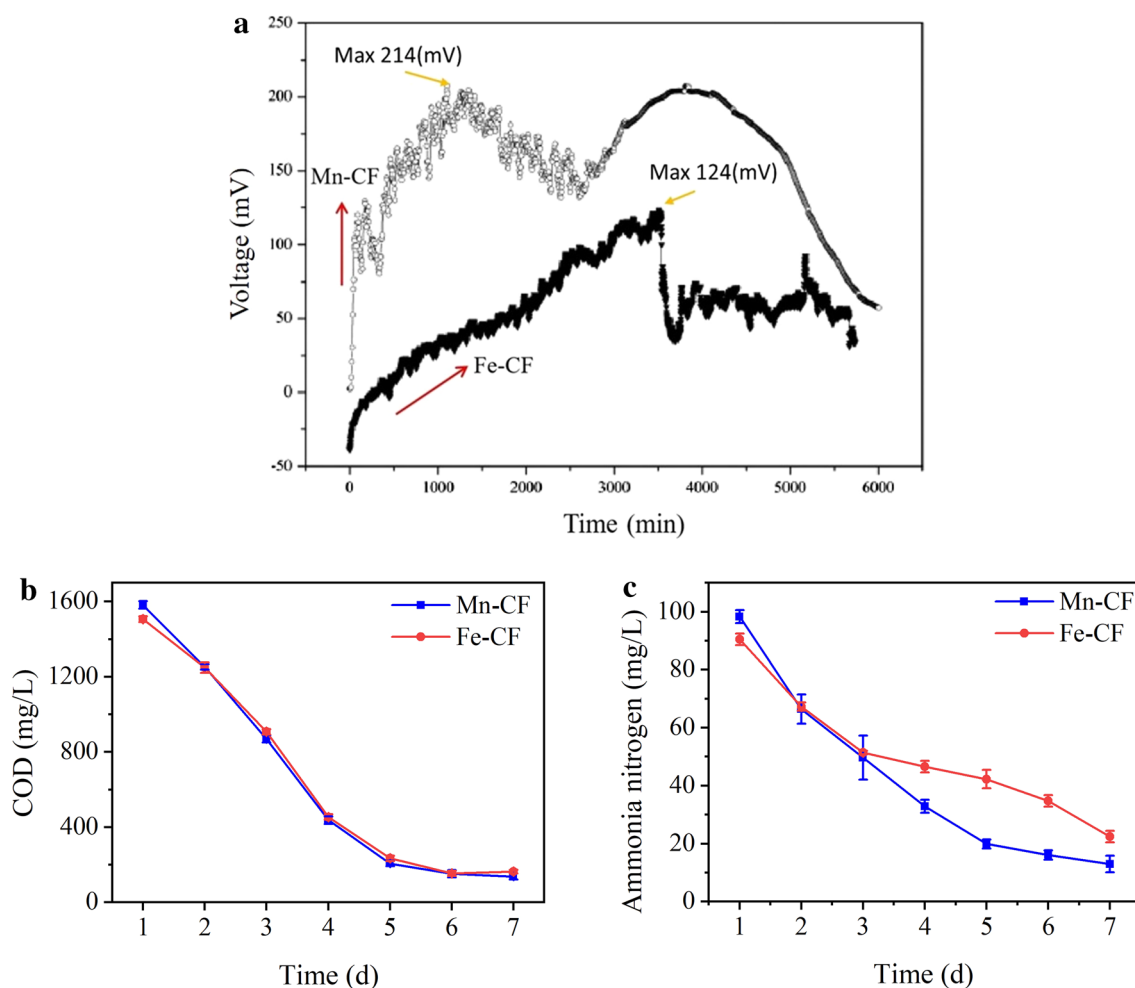


Fig. 2 Comparison of (a) power generation, (b) chemical oxygen demand (COD) removal and (c) ammonia removal for manganese ore-modified carbon felt (Mn-CF) and magnetic ferroferric oxide-modified carbon felt (Fe-CF) electrodes.

Note that the manganese ore-modified carbon felt (Mn-CF) electrode has the highest voltage and the fastest rise, but the removal effect is similar for both electrodes

felt electrode and 89.5% for the magnetic ferroferric oxide-modified carbon felt electrodes. The removal of ammonia nitrogen by the manganese ore-modified carbon felt electrode (84.5%) is slightly higher than that of the magnetic ferroferric oxide-modified carbon felt electrode (72.2%). Some scholars have improved the activity of microbial fuel cells by electrodepositing manganese dioxide on the anode, with chemical oxygen demand removal rates reaching close to 100% and generating more electricity (Phonsa et al. 2018). By using activated carbon combined with iron and nitrogen carbon nanospheres as cathodes, the chemical oxygen demand removal rate of 80.2% could be achieved (Zhang et al. 2021). It has been proposed that MnO_2 can act as a redox mediator to accelerate the electron transfer between microbial cells and pollutants, thus facilitating the removal of pollutants (Che et al. 2021). Other metal oxides in manganese ore increase the surface roughness and specific surface area of the electrode; the manganese ore-modified carbon

felt electrode can be loaded with more microorganisms (Zhang et al. 2014). For the magnetic ferroferric oxide-modified carbon felt electrode, the magnetic ferroferric oxide itself is superparamagnetic and the trivalent iron can be used as an electron acceptor for microbial metabolism. Microorganisms can use Fe^{2+}/Fe^{3+} as a redox mediator to accelerate the decomposition of organic matter in microbial fuel cells (Lovley et al. 2004). Therefore, although the manganese ore-modified carbon felt electrode is slightly more effective than the magnetic ferroferric oxide-modified carbon felt electrode for pollutant removal, the removal rates are relatively close.

Treatment effects of dual-chamber wastewater microbial fuel cells and optimization of ammonia recovery

The manganese ore-modified carbon felt electrode was used as the anode of the dual-chamber microbial fuel

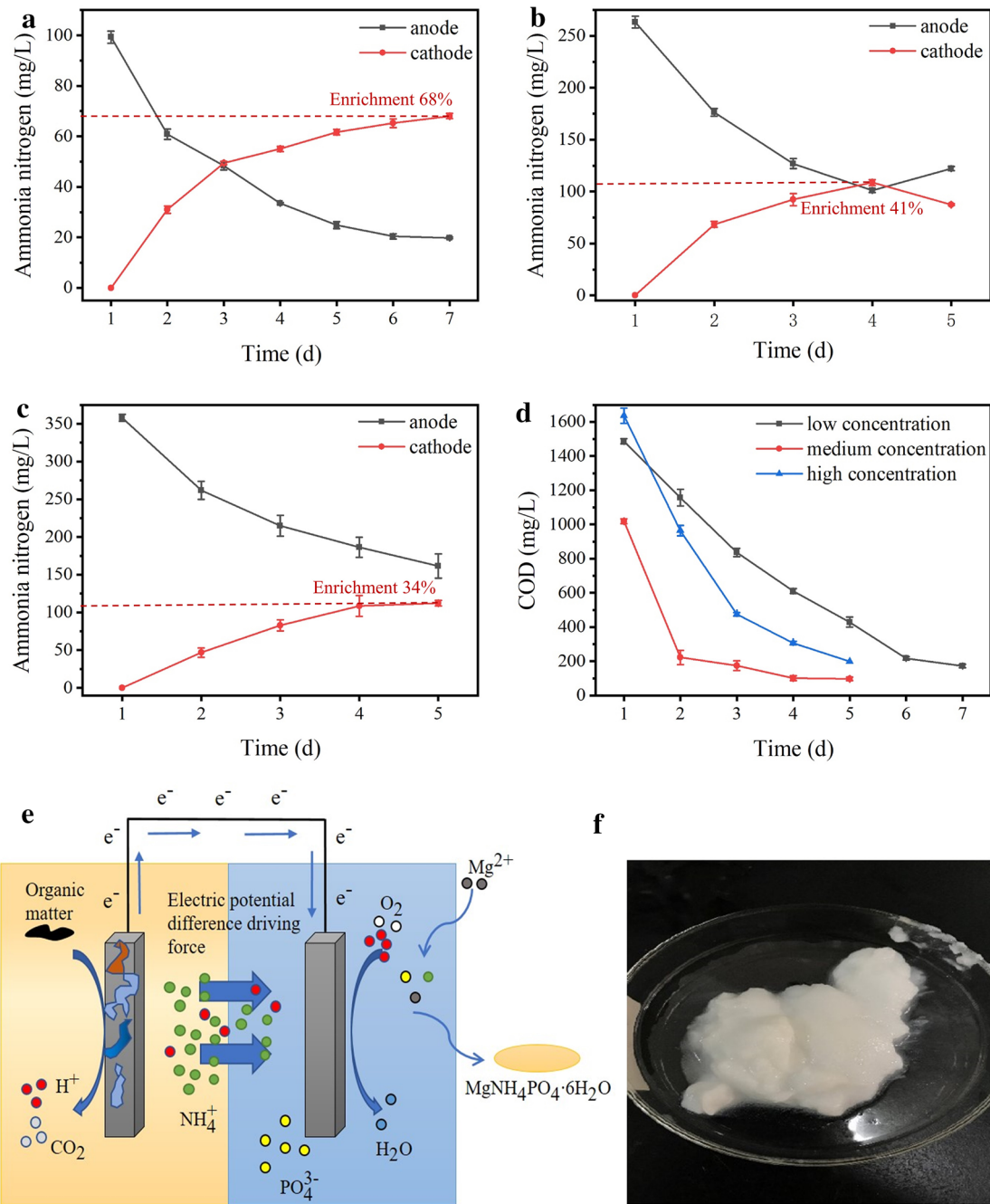


Fig. 3 Comparison of ammonia recovery and ammonia nitrogen transfer effect and chemical oxygen demand (COD) removal effect under different influent ammonia concentrations: **a** low concentration, **b** medium concentration, **c** high concentration, **d** removal effect,

e mechanism of struvite recovery, **f** struvite successfully recovered from the cathode chamber. Note the transfer rate of ammonia nitrogen is the highest under low concentrations

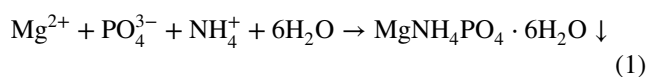
cell. The effects of different influent ammonia concentrations on its performance were investigated. The results are shown in Fig. 3. Under low concentration of influent ammonia, the ammonia enrichment rate of the cathode chamber reached 68% which was higher than that of the medium concentration condition (41%) and the high concentration condition (34%). The chemical oxygen demand

removal rate reached 86.7% at low concentrations, 90.5% at medium concentrations and 87.1% at high concentrations, respectively. The low concentration of influent ammonia is more favorable for the enrichment of ammonia nitrogen in the cathode chamber.

The transfer of ammonia from the anode chamber through the proton membrane to the cathode chamber is

mainly driven by the potential difference and concentration difference (Kim et al. 2008). Under medium concentration conditions, the excellent redox performance and low electron transfer resistance of the manganese ore-modified carbon felt electrode enabled the microorganisms to degrade the organic carbon source in the early stage rapidly. In this case, the chemical oxygen demand removal reached 76.0% on the first day. These two properties lead to a low organic carbon source during the reaction, which generates low electric field forces in the late stage and therefore does not promote ammonia transfer effectively. Under high-concentration conditions, the organic carbon source is sufficient. But the ammonia nitrogen transfer rate is still relatively low. This is probably because the high concentration of ammonia nitrogen has a negative effect on microorganisms, thus leading to the insufficient electric field driving force (Puig et al. 2010). Therefore, the manganese ore-modified carbon felt electrode is more favorable for the enrichment and potential recovery of ammonia nitrogen in the cathode chamber. Meanwhile, its removal rate of chemical oxygen demand remains high under low concentration of influent ammonia.

We conducted further investigations to enrich ammonia at the cathode using the driving effect of electric field force. In particular, we added a phosphate buffer to the cathode to enrich the cathodic medium in ammonia and phosphate ions. Then, to ensure the removal of ammonia nitrogen and to avoid wasting buffer solution, magnesium ions were added to the cathode chamber for the recovery of struvite (Fig. 3e). The reaction is:



According to Eq. 1, a 1:1:1 molar ratio of magnesium ion, phosphate ion and ammonia ion allows optimal precipitation of struvite. Therefore, after complete reaction of ammonia nitrogen at low concentrations, we transferred 50 mL of cathode solution into a beaker, adding magnesium sulfate heptahydrate, stirred magnetically, settled for 5 min and recovered struvite by filtration (Fig. 3f). Ammonia was found undetectable in the filtrate. Therefore, our method allow complete recovery of ammonia nitrogen as precipitated struvite from the cathodic medium of the dual-chamber microbial fuel cell.

Ammonia nitrogen was successfully recovered at the cathode, which is beneficial to the recycling of resources. This work presents a method of using modified electrodes to recover resources in microbial fuel cell treatment of black water. This can generate electricity and recover ammonia nitrogen while removing chemical oxygen demand in black water. If this approach can be improved

and expanded, then microbial fuel cells can recover more resources and will relieve resource pressure.

Conclusion

A manganese ore-modified carbon felt electrode was successfully prepared. This electrode has excellent redox performance and lower polarization resistance that is more favorable for electron transfer, which brings about better power generation. The maximum voltage of the manganese ore-modified carbon felt electrode is 1.7 times higher than that of the magnetic ferroferric oxide-modified carbon felt electrode. Meanwhile, the start-up time to reach the maximum voltage is 68% shorter than that of the magnetic ferroferric oxide-modified carbon felt electrode, which can achieve faster start-up of the system. The application of manganese ore-modified carbon felt electrode in microbial fuel cells can improve the removal of chemical oxygen demand and enrichment of ammonia nitrogen when treating black water. Ammonia nitrogen was successfully recovered at the cathode, which is beneficial to the recycling of resources.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10311-022-01490-1>.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Improved electricity production and nitrogen enrichment during the treatment of black water using manganese ore-modified anodes

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Text S1 Microbial fuel cell device size and start-up method

We constructed a dual-chamber and a single-chamber microbial fuel cell. The dual-chamber microbial fuel cell system is made of 0.5 cm thick plexiglas, and the cathode and anode chambers each consist of a square plexiglas containers, and is separated from the anode chamber by a Nafion117 proton exchange membrane. The dimensions of both cathode and anode chambers are 6 x 6 x 6 cm; the anode is sealed and the cathode is aerated with an aeration head. The anode is a 5 x 4 cm modified electrode, and the cathode is a 5 x 4 cm stainless steel wire mesh connected to a 1000 Ω resistor through a titanium wire to form a circuit. The single-chamber microbial fuel cell has the same configuration and dimensions as the dual-chamber device, except without a proton exchange membrane between the cathode and anode chambers.

The single-chamber microbial fuel cell and dual-chamber microbial fuel cell systems were started simultaneously using intermittent water influx. The start-up was performed by the open-circuit constant potential start-up method by disconnecting the external circuit of the microbial fuel cell and applying a constant -300 mV DC potential to the anode. For the initial start-up, the anode chamber of both the single-chamber microbial fuel cell and the dual-chamber microbial fuel cell were inoculated with cultured anaerobic sludge at 30% of the effective reactor volume. Then, simulated black water was added and aeration was performed near the cathode in the single-chamber and in the cathode chamber of the dual-chamber. During start-up, the nutrient solution was changed every 4 days for the single chamber microbial fuel cell reactor, and the anode nutrient solution and cathode buffer solution were changed every 4 days for the dual-chamber microbial fuel cell. Water samples were collected once a day during start-up to test removal of contaminants. The reactors were placed at room temperature of 20-25°C.

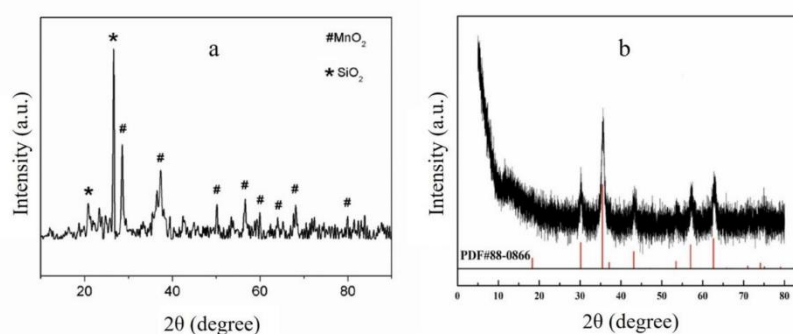


Figure S1. X-ray diffraction analysis results for powdered manganese ore and magnetic ferroferric oxide (a) powdered manganese ore, whose main components are MnO₂, SiO₂ and lesser amounts of other metal oxides, (b) fabricated magnetic ferroferric oxide compared with standard ferric tetroxide (red part), with high peak recombination and consistent peaks

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Table S1. Composition of the simulated black water

Chemicals	Molecular formula	Content
Glucose	C ₆ H ₁₂ O ₆	0.7 g/L
Sodium acetate trihydrate	CH ₃ COONa·3H ₂ O	1.6 g/L
Ammonium Chloride	NH ₄ Cl	0.3 g/L
Potassium Dihydrogen Phosphate	KH ₂ PO ₄	0.044 g/L
Trace element stock solution	The ingredients are listed in Supplementary Table 2	1mL/L

Table S2. Composition of the trace element stock solution

Chemicals	Molecular formula	Content
Ferric chloride	FeCl ₃	0.90 mg/L
Zinc Sulfate	ZnSO ₄ ·7H ₂ O	0.12 mg/L
Sodium molybdate	NaMoSO ₄ ·2H ₂ O	0.06 mg/L
Manganese Chloride	MnCl ₂ ·4H ₂ O	0.06 mg/L
Potassium Iodide	KI	0.18 mg/L
Copper sulfate	CuSO ₄ ·5H ₂ O	0.03 mg/L
Calcium chloride	CaCl ₂ ·6H ₂ O	0.15 mg/L
Boric acid	H ₃ BO ₃	0.15 mg/L

Table S3. Material composition for preparation of the modified electrode

Electrodes	manganese ore powder/magnetic ferroferric oxide	acetylene black	polyvinylidene fluoride
0.5g manganese ore-modified carbon felt	0.4g	0.05g	0.05g
1.0g manganese ore-modified carbon felt	0.8g	0.1g	0.1g
1.5g manganese ore-modified carbon felt	1.2g	0.15g	0.15g
0.5g magnetic ferroferric oxide-modified carbon felt	0.4g	0.05g	0.05g
1.0g magnetic ferroferric oxide-modified carbon felt	0.8g	0.1g	0.1g
1.5g magnetic ferroferric oxide-modified carbon felt	1.2g	0.15g	0.15g

Table S4. Polarization resistance values of different electrodes in microbial fuel cell

Electrodes	Polarization resistance values (Ω/cm ²)
Carbon felt	2.0
0.5g manganese ore-modified carbon felt	1.0
1.0g manganese ore-modified carbon felt	2.2
1.5g manganese ore-modified carbon felt	2.0
0.5g magnetic ferroferric oxide-modified carbon felt	3.5
1.0g magnetic ferroferric oxide-modified carbon felt	2.0
1.5g magnetic ferroferric oxide-modified carbon felt	3.5

Note: Polarization resistance results are simulated by the Zview impedance fitting software