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Effects of Ni nanoparticles, MWCNT, and MWCNT/Ni on the power production and the wastewater treatment of a microbial fuel cell

Ramesh Aryal[a], Diana Beltran[b], and Jia Liu[a]

[a]Department of Civil and Environmental Engineering, Southern Illinois University, Carbondale, IL, USA; [b]Department of Physics, Southwestern University, Georgetown, TX, USA

ABSTRACT

Ni nanoparticles (NPs), multi-walled carbon nanotubes (MWCNT), and MWCNT/Ni were compared for the first time in enhancing power production and wastewater treatment efficiency of a two-chambered microbial fuel cell (MFC). The cathode electrode – a 3D carbon fiber brush – was modified for the first time using different amounts of the three types of nanomaterials. Closed-circuit voltage of the cell was recorded, and chemical oxygen demand (COD) of the anode solution was measured with time. The overall performance of the MFC was enhanced in the following order: MWCNT > MWCNT/Ni > Ni. The power production increased by 7.9 times to 1.2 W/m^3 with 1.5 mg/cm^2 of MWCNT. The power density further increased to 1.9 W/m^3, and the COD maximally decreased by 163.3 mg/L in a 24-h duration with 3.0 mg/cm^2 of MWCNT. The internal resistance decreased maximally by 65.2% to 0.4 kΩ with 1.5 mg/cm^2 of MWCNT/Ni, and further to 0.3 kΩ with 3.0 mg/cm^2 of MWCNT/Ni. Electrochemical impedance spectroscopy (EIS) was conducted to assess the effects of different nanomaterials on the impedance of the MFC. Charge transfer resistance of the cathode was maximally reduced by ~85% to 0.3 Ω with 3.0 mg/cm^2 of MWCNT/Ni. Considering price, stability, and performance, MWCNT is the most practical material for cathode modification. This study is meaningful for sustainable wastewater treatment by enhancing energy production from wastewater treatment process through applying low-cost nanomaterials on the cathode of the MFC.

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Microbial fuel cell; wastewater treatment; power production; Ni nanoparticles; MWCNT; electrochemical impedance spectroscopy

1. Introduction

The necessity of low-energy and cost-effective wastewater treatment has never been greater than this moment of time. Depletion of fossil fuels, water shortage, and environmental pollution have driven the scientific community to look for sustainable wastewater treatment method. At current scenario, wastewater treatment processes are predominantly energy-intensive and require high investment and operating costs. The challenges faced by existing technologies have brought the wastewater industry on the verge of paradigm shift in viewing wastewater as a resource from which energy can be generated rather than waste that needs to be treated. It is estimated that municipal wastewater contains approximately 9.3 times more energy than currently needed for its treatment in a modern municipal wastewater treatment plant (WWTP) (Li, Yu, and He 2014). Microbial fuel cells (MFCs) have the potential to be used for converting chemical energy stored in wastewater to electrical energy and yield cost savings (Heidrich, Curtis, and Dolfing 2010; Oh et al. 2010; Pandey et al. 2016).

MFC is a recently developed bioelectrochemical system which can be used for energy recovery. It has been applied to generate electricity from wastewater or biomass through a combination of microbial metabolic and electrochemical processes (Logan et al. 2006; Muthukumar and Sangeetha 2014; Rabaey and Verstraete 2005). Several factors that have impact on MFC performance include: nature of electrode material, distance between the electrodes, substrate, design of the reactor, ion exchange membrane, and properties of catalyst on the electrode (Ghangrekar and Shinde 2007; Kim et al. 2011; Oh and Logan 2006; Pandey et al. 2016; Pant et al. 2010). Catalyst always plays a significant role in the performance of the MFCs (Birry et al. 2011; Morris et al. 2007). Different types of catalysts have been applied on the cathode surface to enhance the performance of MFCs (Kim et al. 2011; Kodali et al. 2018; Nitisoravut, Thanh, and Regmi 2017). Transition metal nanoparticles (NPs) are effective catalysts for chemical transformation because of their large surface area and the unique combination of reactivity, stability, and selectivity (Li and El-Sayed 2001; Mahmoud et al. 2011). Another material often used in combination with transition metal is multi-walled carbon nanotubes (MWCNTs), which are good conductors of electricity, and have very large surface areas to improve the electrochemically active surface areas and the number of active sites for the performance of the transition metal catalysts (Sun et al. 2010; Tsai et al. 2009).

Transition metal NPs such as Fe, Ni, and Fe/Ni improved the power production of MFCs (Chang et al. 2014; Liu and Vipulanandan 2017; Proietti et al. 2011). Pt-M/C (M = Ni, Co, Fe) catalysts improved power generation in MFCs without affecting chemical oxygen demand (COD) removal from

CONTACT Jia Liu jialiu@siu.edu Department of Civil and Environmental Engineering, Southern Illinois University, 1230 Lincoln Dr., Carbondale, Carbondale, IL 62901, USA

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sewage (Chang et al. 2014). Carbon supported Ni phthalocyanine – MnO_x composite and Ni phthalocyanine modified cathode enhanced performance of MFCs (Tiwari, Noori, and Ghangrekar 2017). Al/Ni NPs with dispersed carbon nanofiber were used for the electrochemical reduction of Cr(VI) in water and simultaneous bioelectricity generation (Gupta, Yadav, and Verma 2017). Ni NPs – doped carbon film, prepared by carbonization, improved power density due to synergistic effect of graphite carbon nanofibers and Ni NPs (Khare, Ramkumar, and Verma 2016). Similarly, non-precious metals such as Co, Ni or Fe, and MnO_2 coated carbon nanotubes have been used as cathode catalysts to improve MFC performance (Bosch-Jimenez et al. 2017; Valipour, Ayyaru, and Ahn 2016; Zhang et al. 2011; Zhao, Watanabe, and Hashimoto 2013).

Surface area of electrode also plays a significant role in the power production of MFCs. Better performance of MFCs was achieved with activated carbon cathodes due to the high surface area of the material (Srikanth et al. 2016; Zhang et al. 2009). MFC fabricated with ß-MnO_2/carbon nanotubes had better performance owing to its higher surface area, larger pore diameter and great pore volume (Jiang et al. 2017). In addition, electrode modified with nanomaterial, especially MWCNT, created higher surface area that allowed increased charge transfer from anode solution to electrodes, and the power production was increased from 168.5 mW/m^2 of the control (electrode without modification) to 267.8 mW/m^2 (Mohanakrishna, Mohan, and Mohan 2012). Nanomaterials have far larger surface areas than similar masses of larger-scale materials, their usage in electrode modification would potentially increase electrode surface area, that would lead to increased power production.

In addition, high internal resistance is a critical factor that impedes the power production of the MFCs (Fan, Sharbrough and Liu 2008; He et al. 2006). The internal resistance in an MFC decreases with the use of catalysts on the electrode surface (Wen et al. 2012). Electrochemical impedance spectroscopy (EIS) analysis revealed reduction in charge transfer resistance of a carbon cloth electrode modified by conductive polyaniline nanoflowers, which resulted in 2.6 and 6.5 times higher voltage and power output, respectively, than pristine carbon cloth electrode (Liu et al. 2017). Thus, the effects of nanomaterials on total internal resistance, as well as on charge transfer resistance of the electrodes of MFCs worth further investigation.

In this study, the effects of cathode modified by three types of nanomaterials – Ni NPs, MWCNT, and combination of MWCNT/Ni – on the performance of MFCs were analyzed in terms of cell potential, power density, internal resistance, and cathodic charge transfer resistance. These three types of nanomaterials have been studied individually previously; however, as the experimental conditions were different, it was hard to compare the effects of these nanomaterials. In this paper, comparative evaluation of these nanomaterials was conducted for the first time under the same experimental condition. Besides, previously, nanomaterials have been coated on 1D and 2D carbon-based materials, such as graphite, carbon paper, carbon cloth, carbon felt, and carbon fiber (Luo and He 2016; Nitisoravut, Thanh, and Regmi 2017; Wen et al. 2013), it was the first time that nanomaterials were coated on 3D carbon material, i.e., a carbon fiber brush in this study, to enhance the performance of the MFC. In addition, two different dosages of these nanomaterials were applied on cathode surface with hypothesis that MFC performance would be enhanced by increasing the dosage of nanomaterials. Finally, anode performance, quantified by COD reduction during wastewater treatment under influence of the nanomaterials, which is rarely studied, was also investigated.

2. Material and methods

2.1. Production of nanomaterials

Ni NPs were produced by the precipitation pathway (Srinivasan 2007). The electrical resistivity of Ni is 7.0×10^{-8} Ω·m at 20°C. For the production of Ni NPs, 1.3 g of $NiCl_2 \cdot 6H_2O$ was initially mixed with 0.25 g of cetrimonium bromide in 440 mL of deionized water. After that 0.3 g of $NaBH_4$ in 10 mL of deionized water was added dropwise, which resulted in the formation of Ni NPs (Equation. (1)). These Ni NPs precipitated in the bottom of the reactor. The whole experiment was conducted in nitrogen environment with continuous stirring. Once the reaction was completed, several drops of acetone were used to break the foams generated during the reaction, and the NPs were allowed to settle for 1 day. The next day the solution was washed 7–8 times with acetone, and the NPs were dried under nitrogen environment. Finally, dry powders of Ni NPs were obtained. MWCNT (>95%, diameter: 30–50 nm, electrical resistivity 1.0×10^{-4} Ω·m at 20°C) was purchased from the U.S. Research Nanomaterials, Inc. To produce MWCNT/Ni, 0.25 g of MWCNT was added in the initial solution containing 1.3 g of $NiCl_2 \cdot 6H_2O$. The formed Ni NPs were allowed to settle on top of the MWCNT. MWCNT/Ni was also dried in nitrogen before use.

$$NiCl_2 + 2NaBH_4 + 6H_2O \rightarrow Ni + 7H_2 + 2B(OH)_3 + 2NaCl \quad (1)$$

2.2. Microbial fuel cell configuration

Carbon fiber brushes (Mill-Rose, Mentor, OH, USA) were used as the anode and cathode in the MFC. The carbon brush had the diameter of 2.5 cm and length of 5.0 cm. In the cathode chamber, carbon brushes coated with nanomaterials were compared with the brush without coating – the control cathode. The carbon fiber was made up of polyacrylonitrile precursor, which was chemically stable and had an electrical resistivity of 1.7×10^{-5} Ω·m at 20°C. Titanium wires were used to connect the electrodes with an external resistor of 1.0 kΩ, the two electrodes were also connected to a data logger (DI-2008, DATAQ instruments, Akron, OH, USA). The titanium wire was 0.25 mm in diameter and had an electrical resistivity of 4.2×10^{-7} Ω·m at 20°C.

Cylindrical bottles (150 mL working volume) were used as the anode and cathode chambers. An anion exchange membrane (AMI-7001; Membranes International Inc., Ringwood, NJ, USA) was used to separate the anode and cathode chambers (Figure 1). The anode chamber was made anaerobic at the start of the experiment by purging nitrogen gas for 10 min, and it was sealed with silicone to keep the whole chamber anaerobic during the experiment. The anode electrode was obtained from a previous

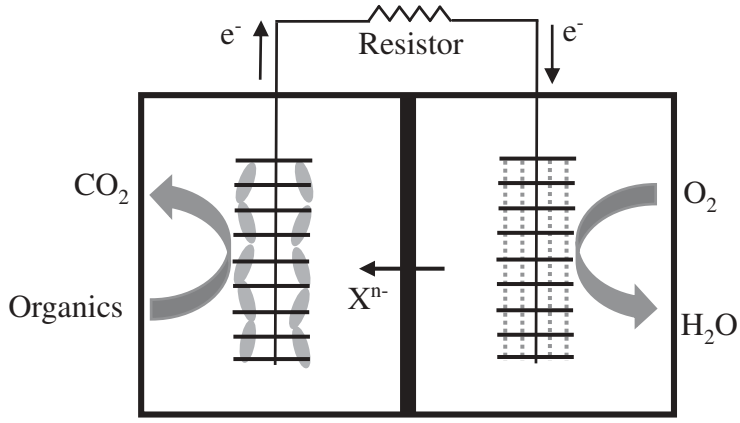

Figure 1. Sketch map of the microbial fuel cell in this study.

MFC which was used for wastewater treatment. Wastewater from an aeration tank in a local WWTP was treated in the anode chamber. The solution in the anode chamber was stirred at 100 rpm (radius = 0.32 cm) with a magnetic stirrer. The medium used in the anode chamber had the following composition: peptone 5.0 g/L, yeast extract 0.5 g/L, K_2HPO_4 1.0 g/L, and KH_2PO_4 0.5 g/L. The purpose of using the medium was to better demonstrate the effect of nanomaterials on improving MFC performance, by potentially supporting rapid growth and high cell yields on the anode (Costa et al. 2002; Thepsuparungsikul, Phonthamachai, and Ng 2012). After acclimation of the electroactive microorganisms on the anode, it was expected that a good electrocatalytic rate of wastewater treatment would be reached without peptone and yeast extract addition, so the running cost would be reduced. The phosphate buffer solution (K_2HPO_4/KH_2PO_4) was used in the cathode chamber. Air was injected in the cathode solution during the whole course of the experiment. The MFC was operated in a fed-batch mode.

Ni NPs, MWCNT, and MWCNT/Ni were applied to the surface of the cathode electrode, respectively. The nanomaterial of either 0.15 or 0.30 g was mixed with 5 mL of Nafion solution (5%; Fuel Cell Earth, Woburn, MA, USA). Carbon brush was dipped into the solution and kept in the fume hood for 2 days until the solution was dried. A layer of coated nanomaterials of 1.5 mg/cm^2 and 3.0 mg/cm^2 (weight of nanomaterials/projected area of carbon fiber brush), respectively, was obtained on the carbon brush for the three different types of nanomaterials, to study the impact of cathode surface area on MFC performance.

2.3. Microbial fuel cell measurement and analysis

In the 7-day period of each batch of experiment, closed-circuit voltage (CCV) was measured using a data logger by connecting to a 1 kΩ external resistor. After achieving a stable CCV, voltage and current were measured by changing the external resistance from 1.0 Ω to 100 kΩ. From the data obtained, the polarization curve and the relationship of power density versus current density were obtained. The maximum power density was obtained when the external resistance was equal to the internal resistance. EIS (Gamry EIS300, PA, USA) was performed to quantify the effect of nanomaterials on the performance of MFC. A small AC signal of amplitude 10 mV was applied to measure the response of the cell with frequency of the signal varied from 30 mHz to 100 kHz. Half-cell impendence of the cathode chamber was measured with the cathode as working electrode, the anode as countering electrode, and Ag/AgCl (saturated KCl, +199 mV vs. standard hydrogen electrode) as reference electrode inserted in the cathode chamber. Similarly, for the measurement of half-cell impedance of the anode chamber, the anode was used as the working electrode, the cathode as the countering electrode, and the reference electrode was placed in the deoxygenated anode chamber. COD was tested by using a UV-vis spectrophotometer (Thermo Scientific BioMate 3S, Waltham, MA, USA). Briefly, 5 mL of the anode solution was mixed with 3 mL of 3.14 mol/L H_2SO_4 containing 10.2 g/L of $K_2Cr_2O_7$ and 33.3 g/L of $HgSO_4$, and 7 mL of 10.0 g/L of $AgSO_4$ in sulfuric acid. The mixture was sealed, fully mixed, and placed at 150°C for 2 h. The absorbance at 600 nm was then measured and compared to the standard curve to determine the COD concentration (Peiravi et al. 2017).

2.4. Nanomaterial and microorganism characterization

The nanomaterials used to modify the cathode electrode, as well as the anode after MFC operation, were observed using a scanning electron microscopy (SEM, FEI quanta FEG 450, Hillsboro, OR, USA) with energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, Concord, MA, USA) in the IMAGE Center at Southern Illinois University Carbondale. The microscopic observation of the nanomaterials was conducted by first spreading them over a carbon tape. A piece of the anode was cut off and dried at room temperature for 24 h before SEM observation. Shape, size, and composition of the nanomaterials were determined. Presence of microorganisms was observed on the anode surface by the SEM.

3. Results and discussion

3.1. SEM observation

SEM results showed that Ni NPs were fiber shaped with an average diameter of ~20 nm (Figure 2a). MWCNT had an average diameter of ~60 nm, and spherical-shaped Ni NPs of

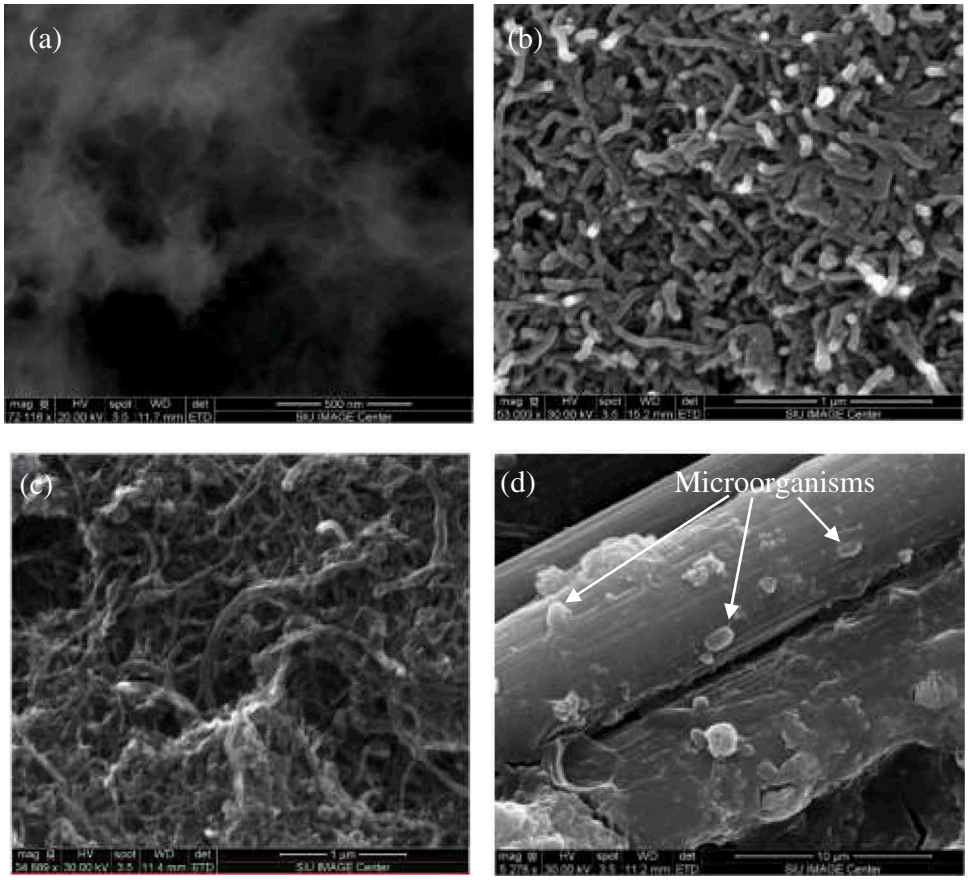

Figure 2. Scanning electron microscopy for Ni nanoparticles (a), MWCNT (b), and MWCNT/Ni (c) used to modify the cathode, and microorganisms on the anode surface at the end of the microbial fuel cell operation (d).

~80 nm in diameter were deposited on top of the MWCNT (Figure 2b,c). EDS analysis showed the presence of Ni, C, and C/Ni in Ni, MWCNT and MWCNT/Ni nanomaterials, respectively (Supplementary Figure 1). The presence of oxygen in Ni NPs was because the Ni NPs were oxidized during the sample preparation for SEM/EDS analysis. Our previous study showed the diameter of fiber shaped Ni NPs were ~25 nm, and Ni element occupied ~56.4% in the observed NPs (Liu and Vipulanandan 2017). One other study on MWCNT supported Ni catalysts reported formed Ni particle size of ~20 nm; however, EDS analysis was not mentioned (Liu et al. 2011). Rod shaped microorganisms (length < 2 μm) were clearly observed at the anode surface at the end of the MFC operation (Figure 2d).

3.2. Effect of nanomaterials on power production

Regardless of the amount deposited on the cathode electrode, all three types of the nanomaterials enhanced the power production of the MFC in this study. The CCV of the MFC with different cathodes had values in the order of MWCNT > MWCNT/Ni > Ni > the control (Figure 3a, 4a). By depositing 1.5 mg/cm^2 of the nanomaterials, the maximum power density was 1,278.2 mW/m^3 using MWCNT, followed by 500.4 mW/m^3 using MWCNT/Ni, 239.0 mW/m^3 using Ni, and 137.1 mW/m^3 using the control electrode (Figure 3b). This result was better than that obtained with Fe and Ni NPs coated cathode (1.5 mg/cm^2), which had the power production of 66.4 mW/m^3 and 57.4 mW/m^3 with Fe and Ni NPs, respectively, compared to the control of 10.6 mW/m^3 (Liu and Vipulanandan 2017). Another study showed that when 0.5 mg/cm^2 of the catalyst was applied, the maximum power density produced from an MFC using Pt-Fe/C cathode was 6.5% higher than that produced using Pt/C cathode of 1030.4 mW/m^2 (Zhang et al. 2011). The internal resistance was 1.3, 0.4, 1.0, and 1.2 kΩ using MWCNT, MWCNT/Ni, Ni, and the control cathode, respectively. The internal resistance was comparable with that reported in the literature of ~0.9 and 1.4 kΩ using Ni NPs and the control carbon fiber brush cathode, respectively (Liu and Vipulanandan 2017). The maximum power density was enhanced by 8.3 times, and the internal resistance was slightly increased when using MWCNT. However, using MWCNT/Ni and Ni, the power density increased by 2.7 times and 0.7 times, and the internal resistance decreased by 65.2% and 11.3%, respectively.

By observation, the cathode coated by Ni, MWCNT, and MWCNT/Ni nanomaterials were green, light black, and greenish black in color, respectively, though the color of the freshly prepared Ni NPs was black. The color change of the Ni NPs was probably because of the formation of Ni_xO_y with

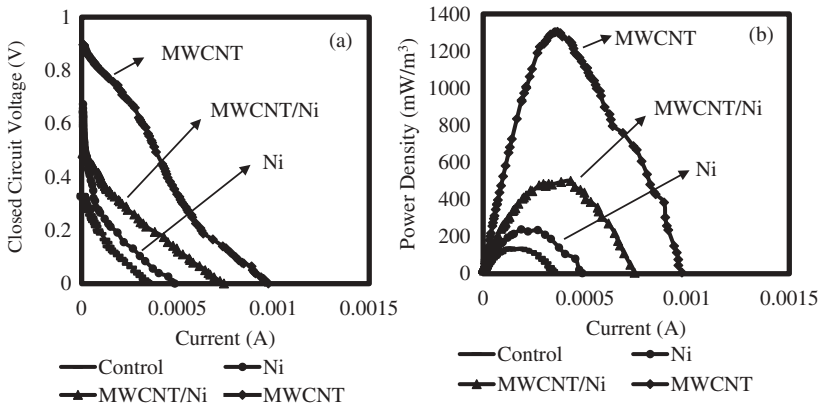

Figure 3. Polarization curve (a) and power density curve (b) for the microbial fuel cell using a cathode modified with 1.5 mg/cm^2 of different types of nanomaterials and compared to the control (without nanomaterials).

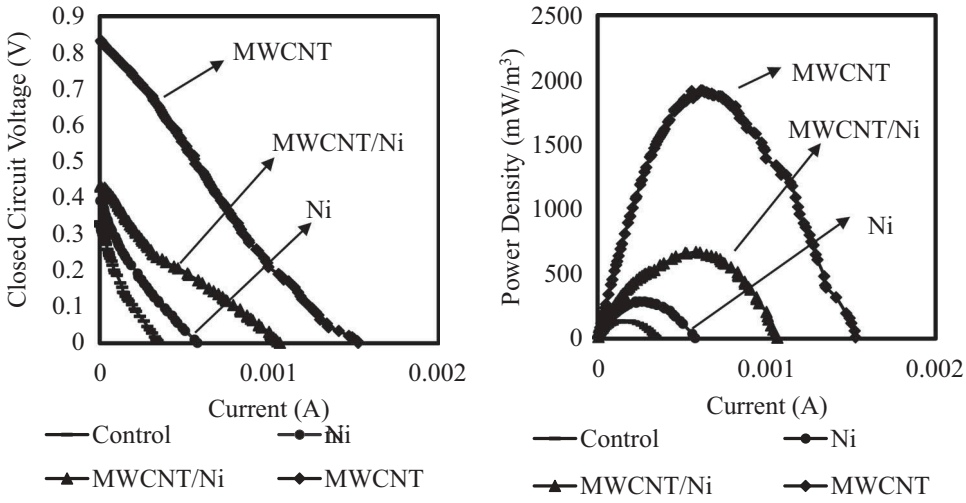

Figure 4. Polarization curve (a), and power density curve (b) for the microbial fuel cell using a cathode modified with 3.0 mg/cm^2 of different types of nanomaterials and compared to the control (without nanomaterials).

time on the surface of the zero-valent Ni submerged in the cathode solution, that was saturated with oxygen. The oxidation of Ni NPs on the cathode changed the properties of the nanomaterial, which probably brought impact on the MFC performance. MWCNT was very effective in enhancing the power production by increasing the current with enlarged electrode surface area; however, it also increased the ohmic resistance of the MFC because of its higher electrical resistivity compared to carbon fiber, the material of the electrode. In comparison, Ni decreased the ohmic resistance of the MFC because of its lower electrical resistivity compared to the carbon fiber. MWCNT/Ni optimally increased the power density with reduction in internal resistance, by increasing the current and the conductivity of the electrode.

By depositing 3.0 mg/cm^2 of nanomaterials, the maximum power density was obtained with MWCNT – 1,918.8 mW/m^3 (Figure 4b), which was 33.4% increase from depositing 1.5 mg/cm^2 of nanomaterials. The maximum power density for MWCNT/Ni and Ni was also increased to 670.8 mW/m^3 and 288.0 mW/m^3, respectively (Figure 4b). The internal resistance was further reduced to 0.8, 0.3, and 0.7 kΩ for MWCNT, MWCNT/Ni, and Ni, respectively. The internal resistances by using 3.0 mg/cm^2 of MWCNT/Ni and Ni were also lower than that obtained by using 1.5 mg/cm^2 of Fe NPs (i.e., 0.7 kΩ) reported in the literature (Liu and Vipulanandan 2017). By increasing the dosage of the nanomaterials, the surface area of the cathode increased, which led to the improved performance of the MFC.

3.3. Effect of nanomaterials on chemical oxygen demand reduction

The treatment efficiency of the MFC was evaluated in terms of COD reduction within a 24-h cycle. The initial COD of the wastewater in the anode chamber was in the range of 1370–1540 mg/L. Results showed the improvement in COD reduction by all three types of nanomaterials with maximum reduction obtained by MWCNT. For 1.5 mg/cm^2 of nanomaterials, MWCNT had maximum COD reduction of 110 mg/L (i.e., 7.4%), which was 4.5 times more than the control of 20.0 mg/L (i.e., 1.3%) (Figure 5a).

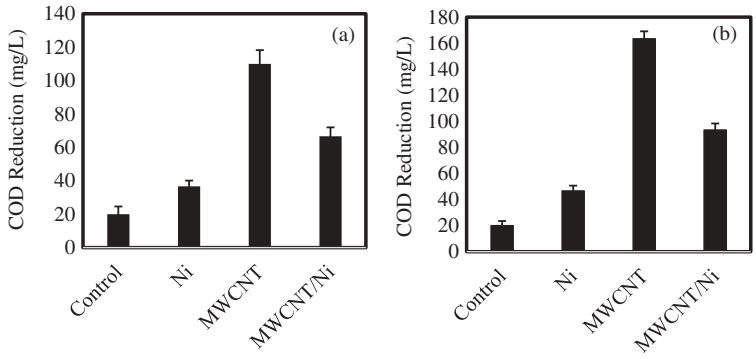

Figure 5. COD reduction per day for treatment of wastewater in the anode chamber of the microbial fuel cell with cathode modified by different types of nanomaterials of 1.5 mg/cm^2 (a) and 3.0 mg/cm^2 (b) in a 24-h duration.

Similarly, Ni and MWCNT/Ni had COD reduction of 36.7 and 66.7 mg/L (i.e., 2.4% and 4.9%), respectively (Figure 5a). For 3.0 mg/cm^2 of nanomaterials, maximum COD reduction obtained was with MWCNT of 163.3 mg/L (i.e., 14.5%), which was 7.1 times higher than the control (Figure 5b), and increased by 48.5% compared to using 1.5 mg/cm^2 of nanomaterials. This increase was also achieved for both Ni and MWCNT/Ni with COD reduction of 46.7 and 93.3 mg/L (i.e., 3.8% and 7.7%), respectively (Figure 5b), which was 27.3% and 40.0% increase compared to results with 1.5 mg/cm^2 of nanomaterials. The increased removal in organic contaminants in the anode chamber was brought by modifying the cathode electrode, which was possibly due to the increased current with using the nanomaterials on the cathode that increased the conversion rate of organic contaminants on the anode electrode. The percentage of COD reduction in this study (i.e., 1.3–14.5%) was based on COD reduction after 24 h of MFC operation. In the literature, the ~80% COD reduction was after 2 weeks' of MFC operation (Ghangrekar and Shinde 2006). For MWCNT modified cathode in this study, with the COD reduction rate, higher COD reduction could be reached after 2 weeks. As the main purpose of this study was to compare the effectiveness of different types of nanomaterials used in cathode modification, the 24-h duration was studied. Besides, the maximum COD (i.e., soluble COD) reduction rate of ~0.2 kg/m^3/day in this study was comparable to or higher than the reported values in the literature (Huang and Logan 2008; Zhang et al. 2013).

3.4. Effect of nanomaterials on internal resistance

With 3.0 mg/cm^2 of nanomaterials (tested at Day 8 of MFC operation), the cathode charge transfer resistance decreased from 2.0 Ω for the control to 1.2, 0.5, and 0.3 Ω for Ni, MWCNT, and MWCNT/Ni, respectively (Figure 6a). Among all the nanomaterials used, Ni was least effective, and MWCNT/Ni was most effective to reduce the charge transfer resistance. Nevertheless, the cathode charge transfer resistance of Ni coated 3D carbon fiber brush in this study was greatly reduced compared to the value of >300 Ω of a piece of carbon fiber sheet (170 cm^2) coated with Ni reported in the literature (Luo and He 2016). The charge transfer resistance of the 3D carbon fiber brush itself was also lower than the value of a 2D carbon cloth (CC, 4 cm×4 cm) of ~250.0, 12.5, and 6.5 Ω for CC, graphene-modified CC, and polyaniline-graphene-modified CC, respectively, due to the increased surface area of the 3D design compared to the 2D design (Wang et al.2018). From our previous study, the lowest cathode charge transfer resistance was obtained by using Fe NPs modified carbon fiber brush of 0.2 Ω, compared to the control of using carbon fiber brush alone of 0.8 Ω (Liu 2014). The decrease in the charge transfer resistance by using nanomaterials indicated the catalytic property of the Ni NPs and the increase in the number of reaction sites by using MWCNT and MWCNT/Ni nanomaterials. Anode charge transfer resistance decreased sharply from 40.0 Ω at Day 0 to 2.3 Ω at Day 4, then decreased slowly to 1.8 Ω at Day 8, and 1.7 Ω at Day 12 (Figure 6b), which would be related to the growth of microorganisms on the anode surface, as observed by the SEM (Figure 2d). Both the nanomaterials and the microorganisms reduced the charge transfer resistances of the electrodes.

The internal resistance is composed of anode impedance, cathode impedance, membrane resistance, anode solution resistance, and cathode solution resistance (Liu and Vipulanandan 2017). Further, the anode or the cathode impedance can be simulated by a constant phase element in parallel with a charge transfer resistance and a Warburg impedance connected in series (Liu, Vipulanandan, and Yang 2018; Sindhuja et al. 2016; ter Heijne et al. 2015). Warburg impedance is the diffusional impedance of the diffusion layer at the electrode surface, it is visible in the Nyquist plot as a straight line with a 45° angle to the abscissa. In this study, both the charge transfer resistance and the constant phase element decreased substantially with time for the anode, which was attributed to the formation of a biofilm layer on the anode surface, and decreased with coating of nanomaterials on the cathode; however, the Warburg impedance, especially for the cathode, did not decrease dramatically, e.g., the cathode and anode impedance for the control were as high as over 100 and 50 Ω, respectively. In addition, the resistance of the membrane was over 100 Ω (Liu and Vipulanandan 2017), thus the total impedance of the cell was ~300 Ω for the MFC using MWCNT/Ni modified cathode, or even higher. One major reason for the high cathode Warburg impedance was that the cathode chamber was not stirred during the experiment, thus the concentration polarization was high due to the presence of a thick diffusion layer.

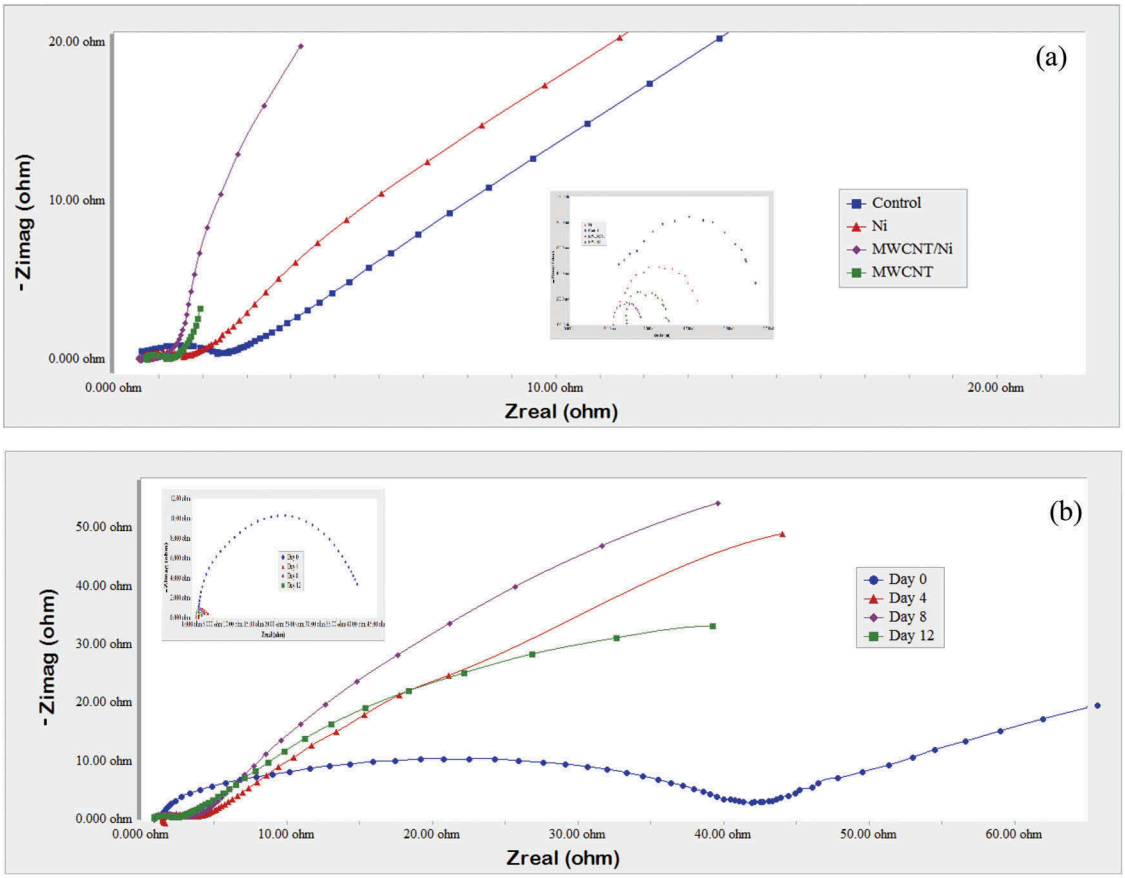

Figure 6. Nyquist plot for the cathode as working electrode, modified by 3.0 mg/cm^2 of different types of nanomaterials, compared to the control after 8 days of microbial fuel cell operation (a), and for the anode as working electrode with respect to time (b).

Stirring the solution in the cathode chamber should minimize the diffusion layer thickness, thus reduce the cathode impedance and the total cell impedance to those values reported in the literature, e.g., ~200 Ω (Fan et al. 2008; Feng et al. 2010).

4. Conclusions

This study compared three commonly used nanomaterials for the first time in modification of the cathode – a 3D carbon fiber brush of the MFC. The following conclusions were advanced. First, the nanomaterials used in this study – MWCNT, MWCNT/Ni, and Ni – all enhanced the power production of the MFC. Second, MWCNT had the highest effect on the performance of the MFC in increasing power production, and MWCNT/Ni had the best performance in decreasing internal resistance, as well as the cathode charge transfer resistance. Third, COD in the anode chamber was studied for the first time under the influence of nanomaterial modified cathode. It was found that the COD was reduced in the same order of the power enhancement: MWCNT > MWCNT/Ni > Ni > the control. Next, higher power production, and lower internal resistance were obtained with increasing the amount of nanomaterials deposited on the cathode. Last, MWCNT/Ni nanomaterial is a promising material in optimally simultaneously improving the properties and the performances of the MFC. However, as Ni NPs are not as stable and cheap as MWCNT: the surface layer of Ni NPs oxidizes with time in water and oxygen environment, and the price of Ni NPs is ~5 times of that of MWCNT, MWCNT is superior than Ni NPs and MWCNT/Ni as a practical material for enhancing performances of MFC – the sustainable wastewater treatment device. This research is meaningful for sustainable wastewater treatment with enhanced chemical to electrical energy conversion during the wastewater treatment process.

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