

Simultaneous phyto remediation of Ni²⁺ and bioelectricity generation in a plant-microbial fuel cell assembly using water hyacinth (*Eichhornia crassipes*)

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Abstract. Plant-microbial fuel cells (PMFCs) are an emerging renewable energy source that can utilize wasted organic matter to produce electricity. In this study, the PMFC technology was hybridized to include phyto remediation of nickel. The main purpose of this study was to determine the effect of combining PMFC technology with phyto remediation of nickel. Three systems were designed for this study. System A is a control for PMFC, system B is a control for phyto remediation, and system C is the combination of the two processes. The combined PMFC and phyto remediation system showed that it has a significantly higher power output than the control (system A). The control PMFC had a maximum power density of 0.29 mW/m², while the hybrid process produced a maximum power density of 0.86 mW/m² which is three times than the output of the control. In terms of the Ni²⁺ uptake, the control recorded a metal uptake of 108.79 µg/g dry weight, lower than the Ni²⁺ uptake of the combined process at 212.42 µg/g dry weight. Overall, the positive results of this study is recommended to be replicated and tested with other plants and heavy metals to establish a new hybrid process of bioelectricity generation and phyto remediation.

1. Introduction

Rapid industrialization fueled by the increasing world population has resulted to an increase in waste production and a decline in non-renewable energy resources. One possible solution is the utilization of renewable energy sources, but preferably those that have a small carbon footprint. An example of such technology are Plant-Microbial Fuel Cells (PMFCs). They are a class under Bioelectrochemical Systems (BES) that utilizes organic matter to produce electricity [1]. Another problem connected with a growing population is proper waste management. Various industrial and commercial sources contribute to water pollution, one of which is a pressing concern is heavy metal pollution. Phyto remediation is presently seen as a feasible way of concentrating heavy metals from wastewater for efficient recovery [2].

Water hyacinth (*Eichhornia crassipes*) has been widely studied as a model plant for aquatic phyto remediation. It is a fast growing aquatic macrophyte that is considered as a weed due to its proliferation in various water habitats all over the world [3]. Several heavy metal uptake values of *E. crassipes* had been reported for a wide variety of metal pollutants such as Cd²⁺, Ni²⁺, Pb²⁺, Ag⁺, and Hg²⁺. In general, the roots of *E. crassipes* accumulate more heavy metals than the shoot, which may be



adsorbed, absorbed, or both [2]. The same plant was also studied for its potential as a model plant in PMFCs, with a maximum power density of 224.93 mW/m² in a benthic system with distillery wastewater as the substrate [4].

It is of interest if a PMFC combined with phytoremediation using *E. crassipes* as a model plant would be feasible in the sense that two independent processes could enhance their collective performance. The results of this study would provide an insight to the feasibility of using hybrid and collective processes to accomplish goals of high importance. If there exists a synergy between phytoremediation and electricity production, the results of this study can be used to develop new efficient processes that accomplish two or more purposes without economic hindrance or undesirably large resource footprint.

The objective of this study is to determine the effect of combining phytoremediation with PMFC technology in the system's electrical generation and the plant's heavy metal uptake. *E. crassipes* was used as the model plant and Ni²⁺ as a representative pollutant.

2. Materials and methods

2.1. PMFC design

The batch PMFC was designed to hold 5 gallons of substrate, and graphite rods (10 mm diameter, 100 mm long) were used as electrodes. The PMFC assembly is shown in figure 1.

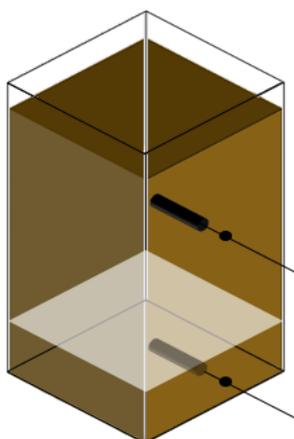


Figure 1. PMFC assembly (A – cotton cloth separator; B – cathode; C – anode)

E. crassipes were sourced from a river in Bulacan, Philippines. Similar-size juvenile plants were selected and acclimated in shallow basins with dechlorinated tap water for 10 days under partial shading. The experiment was also performed under partial shading during the afternoon to avoid the overheating of the system.

2.2. Experimental set-up

Three systems were prepared to accomplish the objectives of the study. System A is a PMFC set-up, with one plant and dechlorinated tap water substrate. System B is a batch phytoremediation system with one plant and a solution of 2.5 ppm NiSO₄. Electrodes were not present in system B to prevent polarization and to simulate *E. crassipes* in a polluted body of water. System C is a PMFC set-up similar to system A, but the substrate is now a solution of 2.5 ppm NiSO₄. All systems were performed in triplicate. A summary of the systems is presented in table 1.

Table 1. Systems studied.

System	Description	Parameters determined
A	PMFC only	Power
B	Phytoremediation only	Ni ²⁺ uptake
C	PMFC + Phytoremediation	Power and Ni ²⁺ uptake

2.3. Data acquisition and analysis

The open circuit voltage and current of systems A and C were measured daily at 12 nm for 21 days using a multimeter. Power and power density values were then determined from the raw data.

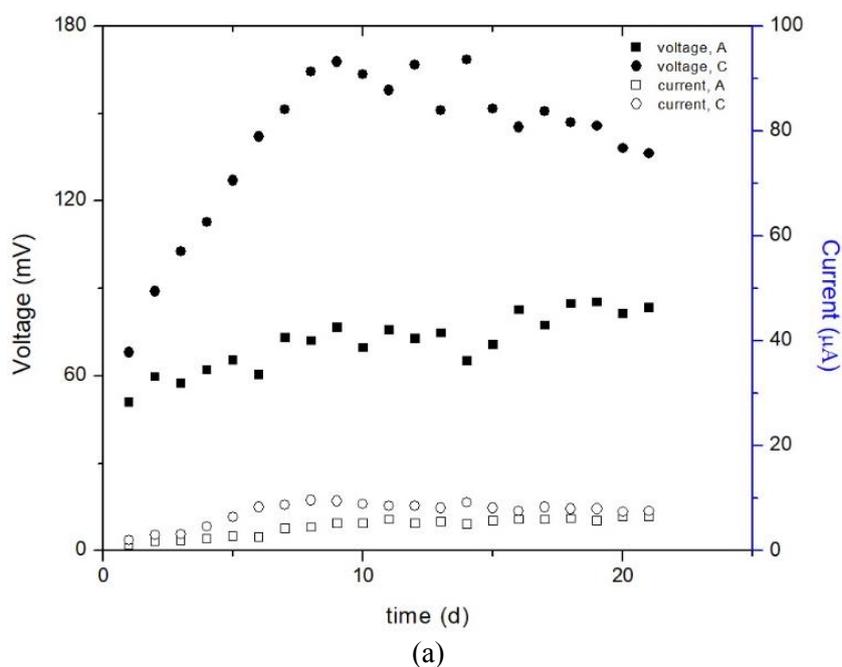
For the determination of Ni²⁺ uptake, whole plants of systems B and C were cut to smaller pieces and oven dried at 100°C until constant weight was achieved. The dried plant samples were cooled in a desiccator, then pulverized in a blender. 1-gram samples were retrieved from the dried powdered plant and digested in heated concentrated nitric acid for 30 minutes until brown fumes ceased to form. The digested solution was twice filtered and diluted to 50 mL. Six standard solutions were prepared and acidified with concentrated nitric acid: 0, 2, 4, 6, 8, and 10 ppm NiSO₄. The standard solutions were used to prepare a standard calibration curve in AAAnalyst 100 Atomic Absorption Spectrometry. The constructed calibration curve was then used to determine the Ni²⁺ concentration in the sample solutions. Ni²⁺ uptake was reported as mg Ni²⁺/g dry weight.

The means of power and Ni²⁺ uptake were compared across systems using two-sample *t*-test.

3. Results and discussion

3.1. Voltage, current, power, and power density

The measured voltage and current and the calculated power of systems A and C are shown for comparison in figure 2.



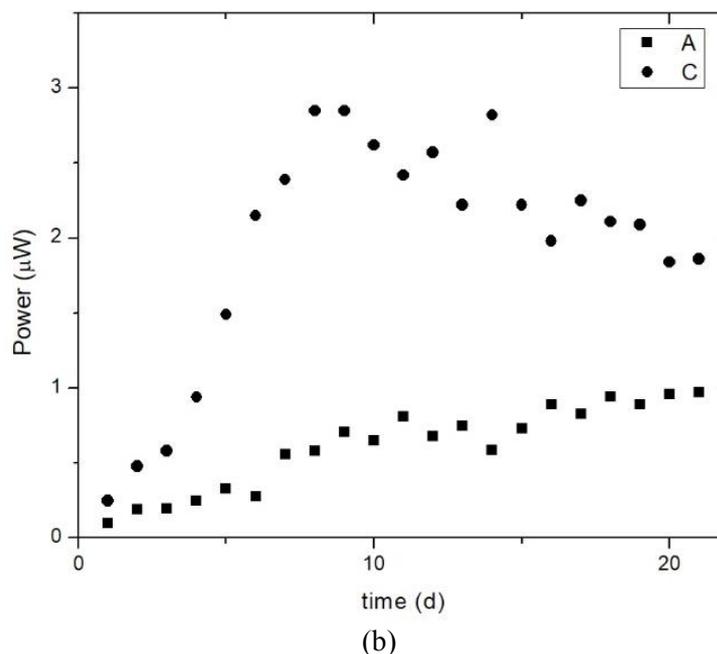


Figure 2. (a) Voltage and current of systems A and C and (b) Power generation of systems A and C.

There is a significant difference between the power output of systems A and C both graphically and statistically ($\alpha = 0.05$). They both exhibited an increase in power output through time, a common characteristic of PMFCs as the bacteria in the roots and substrate begin to colonize the surface of the electrode. System C exhibited a higher mean power output compared to the control (A). One of the possible reasons is the presence of metal ions and miscellaneous charged species in the substrate increases the electrolytic conductivity of the media, thus providing an easier path for the flow of electrons and the exchange of protons. Another possible reason is the utilization of Ni^{2+} by the bacteria in the rhizosphere, although studies dedicated to this are scarce. It has been known that some metal ions inhibit bacterial action like chromium. The observed decrease in power output starting from day 9 can be attributed to physiological changes in the plant and the bacterial population. The same trend was not observed in the control, as such the decrease of power output in system C can be attributed to nickel accumulation.

3.2. Ni^{2+} uptake of *E. crassipes*

After constructing the standard calibration curve, the nickel concentration in the digested solutions were determined. The control (system B) had a concentration of $108.79 \mu\text{g/g}$ dry weight, which is in close agreement with literature values [2]. On the other hand, the phytoremediation system coupled with PMFC posted a higher average metal concentration at $212.42 \mu\text{g/g}$ dry weight, roughly twice the heavy metal uptake of the control.

One possible explanation for the elevated metal uptake is the system polarization. Due to the electrodes in the substrate, continuous charge separation is achieved as electrons and hydrogen ions are continuously exchanged and mobilized. The anode, which is the electrode situated near the roots of the plant, becomes negatively charged as electrons are released from the oxidation of organic matter. Positive ions would tend to migrate to the anode, where it is more available to the roots of the plant even though the bulk concentration is relatively low.

Another possibility is the electrical stimulation of the plant made it absorb more Ni^{2+} , although further studies must be performed before this can be conclusive.

4. Conclusions

This study has demonstrated the feasibility and possible benefits of combining PMFC technology with phytoremediation. From the results of this study, it can be concluded that phytoremediation coupled with electricity generation via a plant-microbial fuel cell assembly increases the performance of both processes. Specifically, the hybrid process outperforms both individual processes in terms of power output and nickel ion uptake.

Reduction in ohmic resistance and the introduction of an alternative terminal electron acceptor are seen as some of the possible reasons for an increased power output in the hybrid process. Also, system polarization, charge separation, and possible physiological changes in the plant brought by electrical stimulation are probable reasons for the plant's increased metal ion uptake.

With the encouraging results of this study, it can be used as a stepping stone for the development of new, novel technology combinations that tackle more than one problem at the same time. It would then be recommended to repeat this study, but with focus on other possible model plants and other heavy metal pollutants.

References

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