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Deciphering biostimulation strategy of using medicinal herbs and tea extracts for bioelectricity generation in microbial fuel cells

Bor-Yann Chen [a, *], Jia-Hui Liao [a], Chung-Chuan Hsueh [a], Ziwei Qu [c], An-Wei Hsu [a], Chang-Tang Chang [b], Shuping Zhang [c]

[a] Department of Chemical and Materials Engineering, National I-Lan University, I-Lan, 26047, Taiwan
[b] Department of Environmental Engineering, National I-Lan University, I-Lan, 26047, Taiwan
[c] University of Shanghai for Science and Technology, Shanghai, 200093, China

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ABSTRACT

This first-attempt study revealed optimal strategy to supplement extracts of polyphenolics-abundant medicinal herbs and *Camellia* tea as electron shuttles (ESs) for stimulating bioenergy generation in microbial fuel cells (MFCs). Apparently, *Camellia sinensis* (L.) Kuntze and *Syzygium aromaticum* were promising electroactive ESs. Moderate temperature (ca. 65 °C) and slightly alkali pHs (~10) were electrochemically feasible conditions for herbal extraction. Optimal contents of polyphenolics-rich herbs and tea extracts with maximal electrochemical activities could be stably obtained. Power density of MFC supplemented with *Camellia* green tea extract could significantly increase ca. 176%, suggesting that green tea extract would be the most appropriate ESs. Total phenolic contents and electron shuttling capabilities were all electrochemically associated. In addition, chemical structure strongly affected whether antioxidant activities of polyphenolics-abundant herbal extracts could be reversibly switched to be electron-shuttling capabilities (e.g., substitution patterns). Hydroxyl substiutuents *ortho* or *para* to each other were very likely promising for electron-shuttling, but not for *meta* substituents. Moreover, bioelectrochemical treatment upon medicinal herbal extracts (e.g., cyclic electron-donating and withdrawing processes) might be inevitably needed for toxicity attenuation to fully express bioenergy-shuttling activities.

1. Introduction

For sustainable exploration of renewable bioenergy, a microbial fuel cell (MFC) is a bioelectrochemical system that directs an electric current obtained from organics oxidation through indigenous electroactive bacteria and/or mixed consortia [1]. As a matter of fact, MFCs still owned certain technical challenges to be overcome to achieve appropriate levels of power generation for practical applications. For example, regarding electrode improvement, surface modification of carbon felt could significantly reduce electron transfer resistance and considerably augment power-generating performance of MFCs. In addition, Gao et al. [2] selected porous polyethylene (PE) sheet with a blended activated carbon (AC) and highly conductive carbon black (CB) layer to develop novel cathodic materials to increase efficiency of air diffusion to cathode for efficient bioelectricity generation. Thus, such MFCs provided more stable and higher power densities compared to unmodified cathode. Moreover, as Hidalgo et al. [3] mentioned, HNO_3 activation and polyaniline-layer modification methods were used to increase roughness and surface area of carbon felt as well as capacity of attached bacteria, resulting in more than 3 fold increase of bioelectricity-generating performance in MFCs. Furthermore, supplementation of metallic catalyst(s) in cathodic solution(s) was also a feasible alternative to augment electron-transfer efficiency in MFCs for effective power generation. As Gajda et al. [4] pointed out, using iron aminoantipyrine (Fe-AAPyr) catalyst as novel cathodic materials could appreciably augment cost-effective power generation of MFCs and reduce biotoxicity potency to bioelectricity-generating bacteria. Due to aforementioned modification, bacterial activity and durability for long-term operation was also stably maintained. Zinadini et al. [5] provided an innovative integrated MFC-membrane separation process (MFC-MSP) for effective wastewater treatment and

* Corresponding author.
E-mail addresses: boryannchen@yahoo.com.tw, bychen@niu.edu.tw (B.-Y. Chen).

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Nomenclature

CV	Cyclic voltammetry
DPPH	2, 2-diphenyl-2-picryl hydrazyl
EC_x	Effective concentration at *x*% response
EIS	Electrochemical impedance spectroscopy
ES	Electron shuttle
ET	Electron transfer
EW	Extract weight
GAE	Gallic acid equivalent
GA	Gallic acid
GCE	Glassy carbon electrode
EC	Epicatechin
ECG	Epicatechin gallate
EGC	Epigallocatechin
EGCG	Epigallocatechin gallate
LB	Luria-Bertani
MFC	Microbial fuel cell
PTFE	Polytetrafluoroethylene
TF	Theaflavins
TPC	Total phenolic concentration

electricity generation. In addition, Zinadini et al. [6] used sulfonated polyethersulfone (SPES)-synthesized (PES/SPES) proton exchange membrane to increase generated power and electric current more than 4 fold compared to Nafion 117. Li et al. [7] also provided Zn-air battery and MFCs coupled with Co species/N-doped carbon (Co–N–C) derived from ZIF-67 to achieve high power densities and long-term stability. Karamanev et al. [8] scaled up a MFC system based upon electron consumption resulting from respiration of chemolithoautotrophic microbes for stable electricity generation (max. 1800 W/m^2) over 4 years. As aforementioned, apparently MFC system improvement via electrode and membrane modification was usually considered to maximize power generation for practicability of MFCs. As Garg and Lam [1] indicated, the efficiency profiles (e.g., power density and output voltage) of fuel cells also highly depend on operation conditions (e.g., current density, pollutant/nutrient supply and anolyte concentration). However, to significantly increase bioelectricity generation, supplementation of electron shuttles (ESs) as mentioned herein to effectively mediate electron transfer was also of great importance.

In fact, rare studies focused on exogenous augmentation of environmentally friendly ESs to considerably reduce mass-transfer resistance and significantly increase power generation in MFCs. That was why this study tended to seek for appropriate supplementation of sustainable ESs for possible means to maximize power generation in MFCs. It was also revealed that redox mediator-aided MFC was energy-saving and economically promising for bioenergy extraction due to effective electron transfer (ET) stimulation [9–12] of such ESs. To consider environmental friendliness, Chen et al. [6] proposed to use natural bioresources (e.g., edible flora) as candidate ES materials to stimulate bioelectricity generation. As a matter of fact, as electrochemically-driven catalysts, ESs are organic chemical(s) that can be reversibly oxidized and reduced to drive ET phenomena for energy extraction to support global lives (e.g., catechol, vitamin B_2-riboflavin). Thus, with augmentation of ESs, enhancement of ET capabilities could automatically escalate the efficiency of redox-mediated pollutant biodegradation and bioelectricity generation for natutral attenuation via electrochemically-steered bioenergy extraction. However, augmentation of artificially synthesized ESs (e.g., neutral red, methylene blue or decolorized metabolites of azo dyes) to elevate rate of pollutant biodegradation is of course not environmentally friendly due to introduction of secondary contaminant(s) for treatment. That is, augmentation of natural ESs would be more ecologically-accepted to minimize impact to global ecosystems. In fact, due to electrophilic characteristics of electron-withdrawing groups, if hydroxyl (–OH) and/or amino ($-NH_2$) substituent(s) were present on benzene ring *ortho* or *para* to each other, such chemical species would strongly exhibit redox mediating characteristics as ESs [12–15]. Moreover, as cyclic voltammetric analyses indicated, hydroxyl substituent(s) seemed to be more electrochemically reversible and stable than amino groups to mediate ET phenomena. That is, when hydroquinone-like chemical structures were present, such chemicals could own promising capabilities to stimulate ET as ESs, increasing the efficiency of electron transport chain in microbial cells. To consider environmental friendliness for sustainable development, inevitably polyphenolics-rich natural bioresources (e.g., medicinal herbs and edible flora) used as ESs should be more electrochemically appropriate and energy-saving for bioenergy extraction in MFCs. For instance, medicinal herbs-*Syzygium aromaticum* (Dīng-xiāng), *Lonicera japonica* (Jīnyín-huā) [16,17] were abundant in polyphenolics and flavonoids antioxidants [18,19]. They should be electrochemically functioning to be manipulated at appropriate conditions as either antioxidants or ESs. Moreover, natural herbs and flora are usually abundant in pigments with radical/electron resonant chemical structures (e.g., auxochrome-based structure). Thus, the presence of such pigments species very likely synergistically interact with electrochemical activities for ET stimulation. Considering electrochemical activities, major constituents of tea extract-catechins could play dual roles to be either antioxidants or ESs [16]. Although Chen and Hsueh [20] proposed conceptual approaches with plausible reasons to suggest abundant edible flora as ESs (e.g., polyphenolics antioxidants as possible ESs) for bioenergy "mining" (e.g., MFCs, electro-fermentation), detailed exploration to uncover such mysteries has still not been implemented, leading to further applications for optimal bioenergy extraction still remained uncertain. Although many literature mentioned characteristics of medicinal herbs and myriads of tea extracts or creams (e.g., antioxidant actives and medical functions), rare studies have been directed towards sustainable electron-shuttling capabilities for renewable energy utilization. To provide bioelectrochemical platform for evaluation upon natural bioresource, MFC was adopted to directly respond bioelectricity-generating characteristics in terms of electric current, quantitatively indicating such technical feasibility as well as optimal operation performance. Moreover, this first-attempt approach clearly deciphered critical conditions to switch non-renewable antioxidant activities to sustainable electron-mediating capabilities for biorefinery and bioenergy recycling afterwards.

2. Materials and methods

2.1. Preparation of edible plant extracts

Medicinal herbs-*Lonicera japonica* (Jīnyín huā), *Syzygium aromaticum* (Dīng xiāng), *Citrus reticulate* (Chénpí) and tea- *Camellia sinensis (L.) Kuntze* (green tea), *Oolong tea*, *Camelliaboreali yunnanica*, *Camellia assamica* (Mast.) Chang 2.5 g were ground to be powdered and then dissolved in 50 mL distilled water and 50% ethanol solution for 65 °C total reflux about 2 h. Then, such mixtures of herbal or tea extract were concentrated via reduced pressure of rotary evaporator. After cooling to ambient temperature, such extracts were centrifuged at 13,000 rpm, 25 °C 10 min to obtain supernatant. Such supernatants were then filtered via 0.2 μm filters (Nylon Acrodisk 13 MiniSpike, 13 mm Gelman Sci.) to