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Hrsg. Prof. Dr. Andrea Kruse

DISSERTATION

Development of Carbon Materials for Microbial Fuel Cells

Musa Bishir

Band 9

Development of Carbon Materials for Microbial Fuel Cells

**Dissertation to obtain the doctoral degree of Agricultural
Sciences (Dr. sc. agr.)**

**Faculty of Agricultural Sciences
University of Hohenheim**

Institute of Agricultural Engineering

submitted by

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DECLARATION

Affidavit

pursuant to Sec. 8(2) of the University of Hohenheim's doctoral degree regulations for Dr. sc. agr.

1. I hereby declare that I independently completed the doctoral thesis submitted on the topic

Development of Carbon Materials for Microbial Fuel Cells

2. I only used the sources and aids documented and only made use of permissible assistance by third parties. In particular, I properly documented any contents which I used - either by directly quoting or paraphrasing - from other works.

3. I did not accept any assistance from a commercial doctoral agency or consulting firm.

4. I am aware of the meaning of this affidavit and the criminal penalties of an incorrect or incomplete affidavit.

I hereby confirm the correctness of the above declaration. I hereby affirm in lieu of oath that I have, to the best of my knowledge, declared nothing but the truth and have not omitted any information.

Tübingen, 11.09.2022

.....
(Place, date)

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(Signature)

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LIST OF UNITS, SYMBOLS & ABBREVIATIONS

Symbols & Abbreviations

MFC	Microbial Fuel Cell
HTC	Hydrothermal Carbonization
HPLC	High-Performance Liquid Chromatography
KOH	Potassium Hydroxide
BET	Brunauer-Emmett-Teller
COD	Chemical Oxygen Demand
NAC	Non-activated Corncob Pyrochar
SAC	Steam-activated Corncob Pyrochar
KAC	KOH-activated Corncob Pyrochar
SA_{BET}	Specific BET Surface Area
PD	Pore Diameter / Å
PV	Pore Volume
ρ	Bulk density / kg m ⁻³ .
$\bar{\sigma}$	Electrical Conductivity / S
ϵ^c	Coulombic efficiency / %
p	Pressure / Pa.
F_g	Weight load / N.
m_w	Mass of added weight / Kg.
g	Earth's acceleration (9.81 ms ⁻²)
A	Piston ground area / m ²
h	Height of the pyrochar sample in glass cylinder / m.
R	Ohmic resistance / Ω .
m	Mass of the sample in kg.
V	Volume of the sample in the cylinder / m ³
CR	Compression ratio
V_{p1}	Volume at applied pressure 1 (blank weight) / m ³
V_{p4}	Volume at applied pressure 4 (weight 10 kg) / m ³
Ag/AgCl	silver/silver chloride

Units

Ω	Ohm
Å	Ångström
L	Litre
S	Siemens
μ	Micro
W	Watt
A	Ampere
V	Volt
Pa	Pascal
N	Newton
Kg	Kilogramm
m	meter
s	second
%	Percent

SUMMARY

Doctoral Candidate: Musa BISHIR

Doctoral Thesis Title: Development of Carbon Materials for Microbial Fuel Cells

There are growing interests in microbial fuel cells (MFCs) for anaerobic bioenergy generation. MFC uses electrodes and organic wastewater as substrate for electrogenic bacteria, to catabolize and generate power. Researchers in this discipline continue to be most interested in finding suitably affordable electrode materials. However, despite the large varieties of commercially available electrodes, only few are suitable for electro-active bacterial colonization, during biofilm formation in microbial fuel cells (MFCs), and most of these electrodes are cost prohibitive. Hence there is need to search for low-cost alternative electrodes for MFCs. The focus of this study was to develop electrodes locally from corncob biomass for application in microbial fuel cells. Pyrochars were produced by pyrolysis (600 °C and a continuous flow rate of 3 NL/min of nitrogen gas for 30 min) and subsequently steam or potassium hydroxide (KOH) activation of the pyrochar at 600 °C were carried out accordingly. Physicochemical, structural, and electrochemical properties of the activated and non-activated pyrochars were determined according to standardized analytical methods. A comparative bioelectricity generation from process water of hydrothermal carbonization (HTC) of spent bear grains (pH = 5.99) and treated–biogas digestate (pH = 7.97), was carried out in dual-chambered MFCs, using graphite rod (non-porous and very low surface area) and the locally developed potassium hydroxide (KOH)–activated corncob pyrochar (KAC) and steam- activated corncob pyrochar (SAC) electrodes. In all the MFC systems of this study, a standard strain of actively dividing cells of the electroactive bacterium *Shewanella*

oneidensis MR-1, which were at logarithmic phase of growth (24 h) was used as inoculum for bioelectricity generation. According to BET measurements, 1626 m² g⁻¹ surface area and 14.74 Å pore diameter were obtained from the KOH-activated pyrochar, which was also the most conductive (0.26 S m⁻¹) carbon material used here. The highest power outputs achieved were 323.8 µW and 316.8 µW from HTC process water with SAC and biogas digestate with KAC electrodes, respectively, at an external load of 47 Ω. The initial Chemical Oxygen Demand (48780 mg / L), Dissolved Organic Carbon (4000 mg / L), and Total bounded Nitrogen (5600 mg / L) of the biogas digestate decreased significantly to 36405, 3610 and 4300 mg / L, respectively, in the MFC with KAC electrodes. A Coulombic efficiency of 75 % was recorded from the MFC operated with treated biogas digestate and KAC electrode in a significantly shorter residence time, making it more efficient than its counterpart with SAC electrode, which had a lower Coulombic efficiency of 64 %. In conclusion, chemical activation of pyrochar with KOH resulted in increased electrical conductivity (EC), pore diameter, and most importantly the material's surface area according to the findings. Therefore, KOH-activated corncob pyrochar holds potentials for producing electrode materials with desirable characteristics for successful application in MFC compared to the non-activated and steam-activated pyrochars of the same biomass.

ZUSAMMENFASSUNG

Doctoral Candidate: Musa BISHIR

Doctoral Thesis Title: Entwicklung von Kohlenstoffmaterialien für mikrobielle Brennstoffzellen

Das Interesse an mikrobiellen Brennstoffzellen (MFC) zur anaeroben Bioenergieerzeugung wächst. MFC verwenden Elektroden und organische Abwässer als Substrat für elektrogene Bakterien, die diese abbauen und Strom erzeugen. Das größte Interesse der Forscher in diesem Bereich gilt nach wie vor der Suche nach geeigneten und erschwinglichen Elektrodenmaterialien. Trotz der großen Auswahl an kommerziell erhältlichen Elektroden sind jedoch nur wenige für die Besiedlung mit elektroaktiven Bakterien während der Biofilmbildung in mikrobiellen Brennstoffzellen (MFC) geeignet, und die meisten dieser Elektroden sind unerschwinglich. Daher besteht die Notwendigkeit, nach kostengünstigen alternativen Elektroden für MFCs zu suchen. Der Schwerpunkt dieser Studie lag auf der Entwicklung von Elektroden aus Maiskolben-Biomasse für den Einsatz in mikrobiellen Brennstoffzellen. Pyrochars wurden durch Pyrolyse (600 °C und eine kontinuierliche Durchflussrate von 3 NL/min Stickstoffgas für 30 Minuten) hergestellt und anschließend mit Dampf oder Kaliumhydroxid (KOH) bei 600 °C aktiviert. Die physikalisch-chemischen, strukturellen und elektrochemischen Eigenschaften der aktivierten und nicht aktivierten Pyrochars wurden nach standardisierten analytischen Methoden bestimmt. Eine vergleichende Bioelektrizitätserzeugung aus Prozesswasser der hydrothermalen Karbonisierung (HTC) von Biertrebern (pH = 5,99) und behandeltem Biogasgärrest (pH = 7,97) wurde in Zweikammer-MFCs unter Verwendung von Graphitstäben (nicht porös und

mit sehr geringer Oberfläche) und den vor Ort entwickelten Kaliumhydroxid (KOH)-aktivierten Maiskolbenpyrochars (KAC) und dampfaktivierten Maiskolbenpyrochars (SAC) durchgeführt. In allen MFC-Systemen dieser Studie wurde ein Standardstamm von sich aktiv teilenden Zellen des elektroaktiven Bakteriums *Shewanella oneidensis* MR-1, die sich in der logarithmischen Wachstumsphase (24 h) befanden, als Inokulum für die Erzeugung von Bioelektrizität verwendet. Nach BET-Messungen ergab sich eine Oberfläche von $1626 \text{ m}^2 \text{ g}^{-1}$ und ein Porendurchmesser von $14,74 \text{ Å}$ für den KOH-aktivierten Pyrochar, der auch das leitfähigste ($0,26 \text{ S m}^{-1}$) der hier verwendeten Kohlenstoffmaterialien war. Die höchsten Leistungen wurden mit $323,8 \text{ µW}$ und $316,8 \text{ µW}$ aus HTC-Prozesswasser mit SAC- bzw. Biogas-Gärgut mit KAC-Elektroden bei einer externen Belastung von 47 Ω erzielt. Der anfängliche chemische Sauerstoffbedarf (48780 mg / L), der gelöste organische Kohlenstoff (4000 mg / L) und der gesamte gebundene Stickstoff (5600 mg / L) des Biogasgärrestes sanken in der MFC mit KAC-Elektroden deutlich auf 36405 , 3610 bzw. 4300 mg / L . Die mit behandeltem Biogasgärrest und KAC-Elektrode betriebene MFC erreichte einen Coulomb-Wirkungsgrad von 75 % bei deutlich kürzerer Verweilzeit und war damit effizienter als ihr Gegenstück mit SAC-Elektrode, das einen niedrigeren Coulomb-Wirkungsgrad von 64 % aufwies. Zusammenfassend lässt sich sagen, dass die chemische Aktivierung von Pyrochar mit KOH zu einer Erhöhung der elektrischen Leitfähigkeit (EC), des Porendurchmessers und vor allem der Oberfläche des Materials führte. Daher hat KOH-aktivierte Maiskolben-Pyrokohle das Potenzial, Elektrodenmaterialien mit wünschenswerten Eigenschaften für eine erfolgreiche Anwendung in MFC herzustellen, verglichen mit nicht-aktivierten und dampf-aktivierten Pyrochars der gleichen Biomasse.

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