

Article

Fabrication and Characterization of Environmentally Friendly Biochar Anode

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Abstract: Electrical power generation by means of electrochemical systems utilizing wastewaters is a global energy challenge tackling technique for which a creation of novel eco-friendly electrode materials is in high relevance. For this purpose a Rhodophyta algae derived activated biochar anode bound with a flaxseeds mucilage binder (5, 10, 20, 30 wt.%) was formed and characterized by thermogravimetric, Brunauer-Emmett-Teller (BET) analysis as well as conductivity and mechanical resistance determination. Activation technique with KOH prior to carbonization at 800 °C of algae was employed to obtain biocarbon with a large surface area. The highest specific surface area of 1298.49 m²/g was obtained with the binder-free sample and had a tendency to decrease with the increase of the binder content. It was estimated that biochar anodes are thermally stable at the temperature of up to 200 °C regardless of binder concentration. The concentration of the binder on the other hand had a significant influence in anodes mechanical resistance and electrical conductance: anode with 30 wt.% of the binder had the highest compressive strength equal to 104 bar; however, the highest conductivity was estimated in anode with 5 wt.% of the binder equal to 58 S/m. It is concluded that anode with 10 wt.% mucilage binder has the optimal properties necessary in MFC utilization.

Keywords: microbial fuel cells; activated biochar; biochar anode; environmentally friendly binder



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1. Introduction

Rapid increase of global demand for energy caused by human population growth as well as conventional fuels depletion and environmental pollution elevates international interest among scientists in development of innovative and clean energy generation technologies [1]. Microbial fuel cells (MFC) are one of the defined techniques that addresses mentioned issues and therefore is an actively investigated method [2]. MFC is a technology employed to produce sustainable energy using various carbohydrates and other organic substrates available in wastewaters [3]. Typically, MFC consists of two electrodes compartments—anode and cathode—that are separated by proton exchange membrane (PEM) [4]. In the MFC approach microorganisms instead of metal catalyst at anode are applied as biocatalysts [5]. Bacteria attached on the surface of anode catalyse oxidation reaction of organic matter present in wastewater to release electrons that are transferred to cathode section through an external circuit [4]. Consequently, originated potential differences in between of anode and cathode create an electrical current—electric power [6]. Assuming, that anode must provide a large surface area for biofilm formation purposes as well as good electrical conductivity to achieve well electron transfer through the MFC system, a negatively charged electrode has a significant role, and therefore, eligible anode materials are actively researched nowadays [7].

Most commonly electrodes used in MFC are carbon-based, including carbon felt, cloth, mesh, graphite materials, etc. due to their cost-effectiveness, good biocompatibility and high conductivity [7]. Considering pressing issues of our time pyrolysis of renewable biomass is a very common way employed to obtain biocarbon based electrodes or supercapacitors. As it is seeking to overcome crucial shortcomings of biochar electrodes in MFC like poor electrical conductivity and insufficient surface area as well as lower porosity [8], biochar is prepared by applying various activation and pre-treatment methods [9]. To obtain more efficiently graphitized carbon with higher porosity, Zha et al. [10] performed research of eggplant-derived biocarbon in advance chemically activated with $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$. Investigation revealed that such activation technique allows to build biocarbon electrodes with maximum surface area of $1181 \text{ m}^2/\text{g}$ and power density of $667 \text{ mW}/\text{m}^2$ in MFC according to a pyrolysis temperature and proportion of the salt used during activation. Tang et al. [11] applied activation with $0.1 \text{ mol}/\text{L}$ $ZnCl_2$ prior to carbonization of kapok fibers and produced biocarbon with the surface area of $848.3 \text{ m}^2/\text{g}$ and power density of $801 \pm 40 \text{ mW}/\text{m}^2$ in MFC, which was even higher compared with platinum-based electrodes. Thus, the approach of biocarbon fabrication by treating bio-mass with an activating agent prior to pyrolysis is a promising way to develop sustainable MFC electrodes avoiding the use of conventional carbon materials.

A considerable amount of research has been carried out using waste biomass as a biochar precursor, for comparison a biomass of higher algae biocarbon used to construct MFC electrodes has been studied to a lesser extent. Although, studies have demonstrated that there is a possibility to fabricate algal biocarbon based electrodes and apply them in MFC technology successfully [12]. Employment of algae biomass for production purposes of value added products is particularly relevant due to the eutrophication process problem that is primary caused by the increase of algae biomass in water sources [13]. Additional advantage of algae utilization in manufacturing of biocarbon electrodes is the one, that cultivation land for growing high yields of algal biomass is not required and it grows with no manpower, naturally in ponds [14]. Wang et al. [12] investigated algal biomass collected on Lake Chaohu, China. Authors applied activation technique with KOH prior to pyrolysis and obtained results demonstrated that algal biochar anode generated 4.1 times higher current density compared with graphite electrode. Yang et al. [1] paper discuss *Chlorella pyrenoidosa* microalgae derived catalysts to coat carbon cloth electrodes applied in MFC technology. In this work an algal biochar catalyst by pyrolyzing a mix of *Chlorella pyrenoidosa* algae, $Mg_5(OH)_2(CO_3)_4$ and $ZnCl_2$ in a mass ratio of 0.67:3:1 was obtained. The results have revealed that carbon cloth electrode covered with produced algal biochar catalyst had a surface area of $636.99 \text{ m}^2/\text{g}$ and generated maximum power density of $2288 \pm 30 \text{ mW}/\text{m}^2$ in constructed MFC system. Activated algal derived biochar, besides the implementation in clean energy generation technologies, provides the perspectives in electrical energy storage technologies as well. For instance, Salimi et al. [15] applied the pretreatment technique by soaking dread *Cladophora glomerata* biomass in 10 mM $FeCl_3$ solution for 300 min prior to slow pyrolysis. By binding obtained biochar with non-toxic polyvinylidene fluoride binder, magnetic electrode with the adequate surface area of $296.4 \text{ m}^2/\text{g}$ and initial specific discharge capacity of $740 \text{ mAh}/\text{g}$ was produced and additional test for energy accumulation technologies showed good relevance. Thus, the activation of algal biomass prior to carbonization is a tool that enables to produce a biochar with desired properties that are relevant in the technology under study.

The biochar obtained after carbonization process is bound using different polymeric binders and thus a durable electrode is formed. Such polyfunctional polymeric binders are of high interest nowadays and are particularly investigated in electrochemical systems [16]. Examples of polymeric binders utilized to construct MFC's anode and cathode are nafion, PDMS (polydimethylsiloxane), PTFE (Polytetrafluoroethylene), PLA (Polylactic acid), PEI (polyethyleneimine), PS (polystyrene), etc. [7]. However, usage of some binders in formation of electrodes is hazardous to the environment and unsustainable. For example, one of the most frequently used aqueous binder PTFE [7] is stabilized by wetting agents

that poses a biological threat due to fluorine containing chemicals [17]. Other commonly used binder perfluorosulfonic acid (nafion) contains this biohazardous element as well [18]; hence, these binder alternatives are considered as undesirable solutions when the aspiration is environmental friendliness. However, natural and eco-friendly binders can also be used for production of electrodes with good electrical properties, although it is little researched. Example of alternative binder was investigated by Wang et al. [19] by carrying out research on carbon-nanotube brush electrodes that were bound with biocompatible and environmentally friendly poly-pyrrole and carboxymethyl cellulose binder. The results have revealed that the prepared composite electrode exhibited well storage properties and good energy outputs with power density of 2970 mW/m^2 generated in MFCs. On the other hand, binder free electrodes are also applicable if it is desired to overcome binder insertion drawbacks such as clogging of pores on the surface of electrode as well as conductivity reduction [20]. For instance, in study conducted by Feng et al. [21] binder-free carbon was derived from sewage sludge pyrolyzing it in the atmosphere of CH_4 and N_2 gases mixture. Anode made of sewage sludge carbon obtained at $1200 \text{ }^\circ\text{C}$ created 5 times higher power density compared to graphite anode which was equal to 2228 mW/m^2 .

Electrode disposal at the end of its shelf life is the issue that directly affects ecosystems due to added harmful binders like nafion and PTFE. Plentiful research has been done on carbon-based MFC electrodes bounded with conventional binders (PTFE, nafion, etc.); however, biochar electrodes bounded with natural and environmentally friendly binders still is a research-lacking field. Therefore, the goal of this study is to investigate properties of MFC electrodes made from seaweed algal biochar with an eco-friendly binder that would be able to decompose naturally without any negative effects to living organisms in the environment.

2. Materials and Methods

An investigation was carried out to verify the feasibility of seaweed derived biochar anode bound with mucilage extracted from flaxseeds as a MFC electrode. Experimental part constituted the fabrication of activated biochar anodes and settlement of obtained anode properties.

In order to evaluate the potential of produced anode utilization in MFC technology, relevant characteristics of produced material were determined. Experimental part of fabricated anode characterisation included thermal, mechanical resistance, specific surface area and conductivity properties identification. Flowchart of designed process is presented in Figure 1.

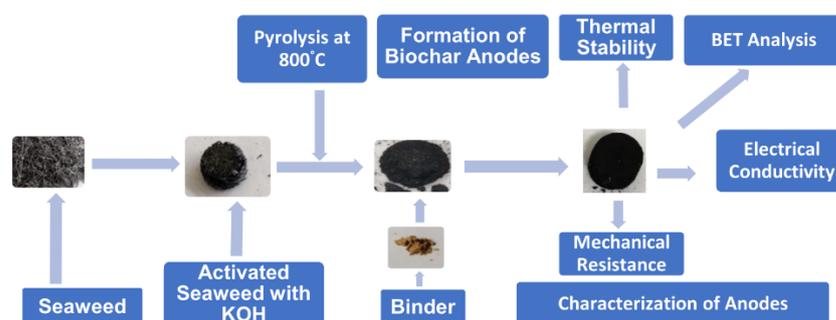


Figure 1. A graphical abstract of all approaches and measurements performed during the investigation.

2.1. Fabrication of Activated Biochar Anodes

2.1.1. Production of Activated Biochar

In this investigation, activated biochar was derived from Rhodophyta seaweed algae that was collected from the Baltic Sea coast in Melnrage, Lithuania. Stored seaweed was carefully washed with distilled water to remove all accumulated sand and other impurities

after-wards drying it at 105 °C for 12 h in a drying oven. Clean and dry biomass was prepared for utilization in activated biochar production.

To obtain highly porous and conductive biochar KOH was chosen as an activating agent. It is estimated that KOH during pyrolysis react with oxygenated species present in biomass and creates numerous amount of cavities in the biocarbon by means of removing oxygen containing groups from the surface. Therefore, the one-step method is mostly employed for activated biocarbon production during which biomass and KOH blend is pyrolyzed at higher temperature compared to the regular one used in biochar fabrication [22].

Activated biochar was produced following the approach described by Wang et al. [12]. Purified, dry algal biomass was grinded to obtain small particles and mixed with solid KOH in the mass ratio of 1:1. Then, the blend was pyrolyzed at 800 °C temperature with a heating rate of 10 °C/min in the inert atmosphere of nitrogen for 3 h. 5% HCl solution was used subsequently to neutralize alkali remained in the obtained carbon and additionally washed with deionized water. Eventually, derived biochar was dried in a drying oven at 105 °C temperature for 12 h.

2.1.2. Mucilage as a Binding Agent Extraction and Preparation

Mucilage was extracted from flaxseed cultivars by following method as described by Ziolkovska et al. [23] with slight modifications. Flaxseeds were not prepared by mechanical grinding prior to extraction process as the grinding would lead to the leakage of other substances and proteins which can reduce the quality of mucilage extract. Since most hull substances from seeds can only partially swell in aqueous media, water is an appropriate solvent in this case. In addition, it is economically feasible to use it for this purpose.

Before the extraction procedure, flaxseeds were washed under running water for 3 min to remove dust from the surface. Flaxseed mucilage was extracted by an aqueous process using distilled water (pH of 7.0) under atmospheric pressure. Firstly, seeds were mixed with hot distilled water (80 °C, 1:25 *w/v* ration) in a glass flask using a continuous magnetic stirrer (400 rpm) for 30 min. The extraction process consisted of two stages. In the first stage, seeds were extracted with distilled water. In the second stage, seeds remaining after the first stage were extracted a second time with a new portion of water. The extract was obtained from the seeds using 200-mesh. The Mucilage was dried to solid content at 105 °C and held in a desiccator until further analysis.

Ball milling technique was employed to obtain fine powder of the mucilage binder. The milling was conducted using Fritsch Pulverisette 6 planetary ball miller. In total 30 milling-pause cycles (milling time—5 min, pause time—30 min, rotation speed—200 RPM) were applied. The diameter of used stainless steel balls was 10 mm, approximate mass of the sample was 1.1 g, and ball to mass ratio was equal to 44 g. Particle sizes of the milled binder were measured using a Hitachi S-3400N scanning electron microscope Figure 2. Particles from 34 µm up to 60 µm in size prevailed, the smallest particles were 8 µm in size.

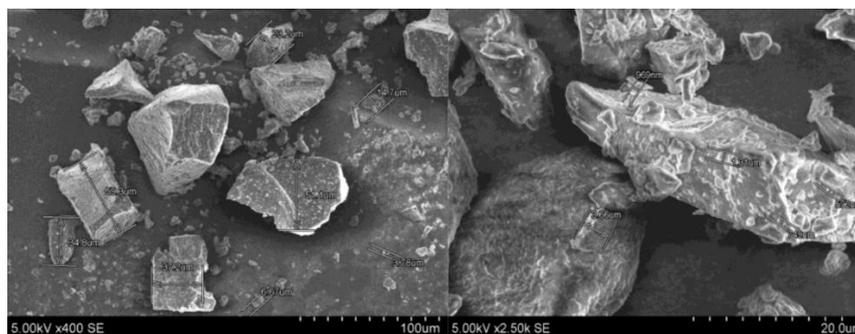


Figure 2. Ball milled mucilage binder particles image obtained employing Hitachi S-3400N SEM with a 5.00 kV energy.

2.1.3. Formation of Anodes

Mixtures of dry activated biochar was prepared with different concentrations (5, 10, 20 and 30 wt.%) of flaxseeds mucilage and named BC5, BC10, BC20 and BC30 respectively. Firstly, fine powder of mucilage was dissolved in deionized water to obtain thick mass similar to glue. The weight amount of mucilage was blended manually with approximately 0.5 mL of water in 30 °C temperature to enhance the solubility of the mucilage. Prepared binding solution was then mixed with grinded activated biochar (particles size was up to 250 µm) obtaining a viscous mass. The mixture was further pressed using 1000 kg/cm force to form cylindrical shape anodes. Eventually, prepared anodes were dried in an oven dryer for 8 h at 70 °C temperature and investigated further.

2.2. Properties Determination of Produced Anodes

2.2.1. Thermal Characterization—Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical approach employed to estimate thermal stability of the matter as well as to determine the formation of volatile compounds during the thermal degradation of a sample by observation of mass change dependent on heating at a stable heating rate [24]. Thermal stability of MFC electrode is an important feature since it is significant to prevent the degradation of thermolabile natural origin compounds in electrodes (in this case—natural binding agent), as the temperature in some cases can reach 50 °C or more during the electrochemical process in MFC [25]. Moreover, the thermal stability test or TGA of the raw material as well as of constructed composite is relevant due to the thorough substance characterization fulfillment.

NETZSCH STA 449 F3 Jupiter analyser with the silicon carbide (SiC) furnace was employed to evaluate thermal characteristics of the stock and obtained activated biochar as well as its mixtures with different concentrations of mucilage binder. Samples of up to 40 mg weight in Al₂O₃ crucibles were heated in 35 °C/min heating rate from 40 °C to 900 °C temperature in the inert atmosphere of nitrogen with a flow rate of 60 mL/min. An isothermal step at 110 °C for 5 min was added to ensure well evaporation of water as well as at 900 °C for 7 min to ensure full vaporization of volatiles and even formation of carbon. Atmosphere was switched to reactive (25 mL/min of compressed air and 35 mL/min of N₂) afterwards and temperature was decreased with the identical heating rate to 800 °C and held at this temperature for an hour to burn out formed carbon completely and evaluate the ash content.

2.2.2. Analysis of Mechanical Resistance

Samples were prepared as described in the section “Formation of Anodes”, although the drying temperature and length of drying was unequal. Prior to analysis of samples mechanical resistance, with distinct concentrations of the binder formed anodes were dried at room temperature (24 °C) for 72 h. Compression tests have been carried out to determine the mechanical resistance of the samples. The compressive mechanical analysis of produced activated biochar anodes were accomplished employing the Zwick Roell universal testing machine with the loading rate equal to 0.5 mm per minute [26].

2.2.3. Brunauer-Emmett-Teller (BET) Surface Area Analysis

Quantachrome Autosorb-iQ-KR/MP automated gas sorption analyser was employed to determine the specific surface area of produced activated biochar and anodes formed with mucilage binder. Surface area characterisation was performed by means of N₂ gases adsorption–desorption isotherms at liquid nitrogen temperature (−196 °C). The specific surface area of samples was calculated with the Brunauer–Emmett–Teller equation. Calculations were performed employing an ASiQwin (Version 2.0) program developed by Quantachrome Instrument 24.

2.2.4. Electrical Conductivity Estimation

Compression molding approach was employed to carry out experiments of resistivity value ($\Omega \text{ m}$) dependence on compression force (kg/cm) applied to the sample based on the methods described by Espinola et al. [27] also Pantea et al. [28]. Cold press technique was implemented operating at a room temperature ($24 \text{ }^\circ\text{C}$) using a two-part mold system Figure 3. Sample of up to 0.5 g weight was placed in a 10 mm diameter cavity of dielectric mould. A rod made of steel was utilized to form cylindrical shape anodes applying pressure from 5 to 60 bar with an increment of 5 bar simultaneously measuring electrical resistance by means of DM3068 RIGOL digital multimeter.

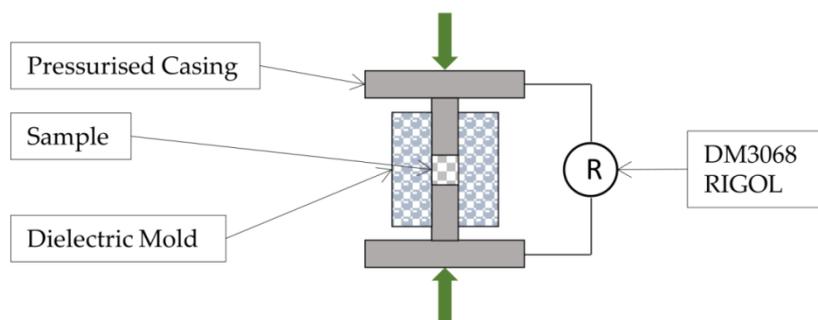


Figure 3. The system of two-part compression mold.

Data of electrical resistance experiments was further utilized in calculations of electrical conductivity. The conductance of bulk biocarbon and fabricated anodes was calculated by means of mathematical expression where electrical conductivity (S/m) is equal to one divided by the measured resistance value ($\Omega \text{ m}$).

3. Results

3.1. Thermogravimetric Analysis (TGA)

The principle of TGA is that the sample loses weight at particular temperatures that indicates the decomposition of a certain component in the sample [29]. Therefore, the thermogravimetry and differential thermogravimetry approaches can be used to characterize composition differences of specific samples. Thermogravimetric curves obtained during the proximate analysis of the red seaweed (Rhodophyta) feedstock is presented in Figure 4. Generally, red seaweed biomass is made of 3 components: cellulose, hemicellulose and lignin, however specifically hemicellulose forms the major part of it, cellulose compiles the smaller part and lignin—the least part. Also, red seaweed normally includes substantial ash as well as relatively high protein content [30].

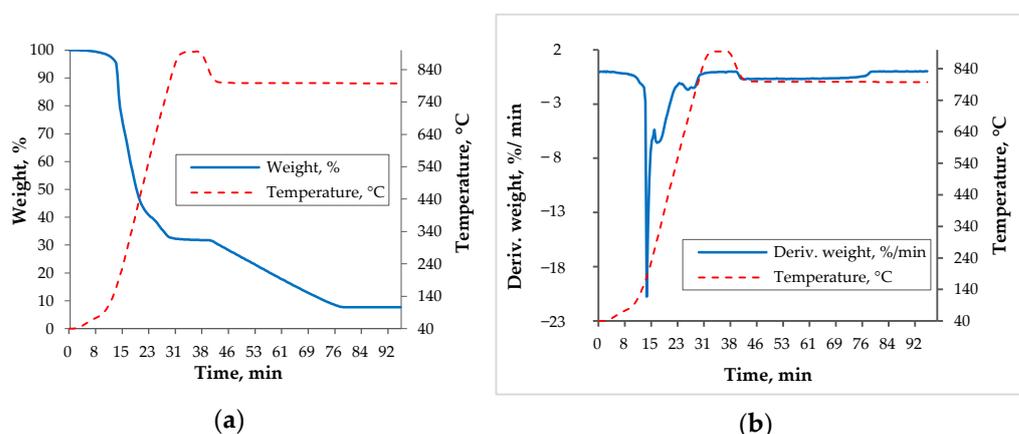


Figure 4. Thermal analysis of red seaweed (Rhodophyta) feedstock: (a) thermogravimetric (TG) curve; (b) derivative thermogravimetric (DTG) curve.

TG curve presented in Figure 4a revealed that moisture composed around 4.62% of the raw material and it evaporated in the temperature range from 40 °C to 168 °C. The thermal decomposition of the material started afterwards and lasted till 900 °C with simultaneous formation of plentiful amount of volatile compounds—around 63.6%. Atmosphere was switched to partially reactive and combustion process started in 39 experiment minute which resulted remaining of 7.71% ash in the crucible eventually.

Peaks in the DTG curve (Figure 4b) illustrated that thermal decomposition occurred in two main points. The first one at around 200 °C reveals the thermal decomposition of hemicellulose [31]; at this temperature disintegration proceeds in maximum speed which indicates that hemicellulose comprises the major part of the investigated algal biomass. The other clear peak at 315 °C stands for cellulose thermal decomposition [31] and the lower reaction rate confirms that it composes much smaller part of the sample. The smaller intensity peak starting at 680 °C can be related to lignin disintegration as its complex structure gives it the highest thermal stability compared with holocellulose components therefore it decomposes at higher temperature [31].

Figure 5 illustrates thermogravimetric curves obtained during the proximate analysis of activated biochar with different concentrations of the binder. Referring to TGA curves in Figure 5a it was estimated that the highest percentage of volatiles have formed during the thermal decomposition of activated biochar with 30 wt.% of mucilage binder that amounted over 27% of total sample weight. Comparatively, the least amount of volatile compounds formed during the degradation of binder-free biochar—around 17.13% respectively. Values of decomposition rates in the partially reactive atmosphere in most cases were even; however, it was determined that decomposition rate of biochar with 10 and 30 wt.% binder concentration in partially reactive atmosphere were distinct compared to other samples. The analysis was accomplished in the micro scale which is performed in great precision when sample is in high homogeneity. From this point the assumption is made that particular biochar samples with the binding agent was roughly heterogeneous and that caused the differentiation in the decomposition rate.

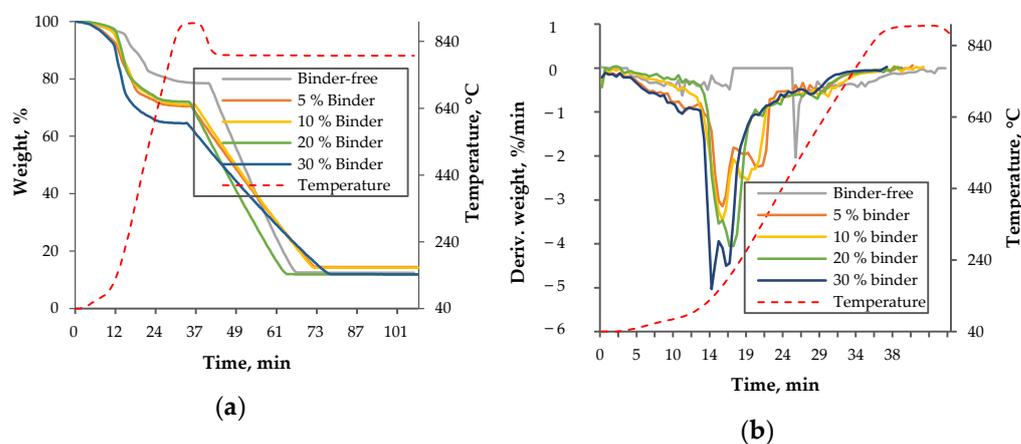


Figure 5. Thermal analysis of activated algal biochar mixed with different concentrations of the mucilage binder: (a)—TG curve; (b)—DTG curve obtained before combustion initiation.

The additional degradation of obtained activated biochar followed by origination of volatiles observed in Figure 5b occurred in the inert atmosphere due to the higher temperature employed as well as more accurate maintenance of constant degradation environment in the proximate analysis compared with the reactor. The higher thermal energy used induced chemical bonds cleavage that were present in organics left in produced biocarbon resulting in the secondary release of volatile compounds. Similar results were also obtained in previous researches and it was confirmed that the lower temperature employed during the pyrolysis to form biocarbon influenced the formation of higher contents of volatiles during the proximate analysis of produced biochar [32].

Table 1 presents the composition differences of samples estimated owing to proximate analysis. It was estimated that in all cases values of remained ash quantities were fairly close, percentages of moisture content were similar as well.

Table 1. Measured moisture, volatile compounds, fixed carbon and ash contents (%) emerged due to the thermal degradation of samples during the proximate analysis employed.

| Sample Name | Moisture (%) | Volatiles (%) | Fixed Carbon (%) | Ash (%) |
|-------------|--------------|---------------|------------------|---------|
| BC0 | 4.40 | 66.01 | 17.13 | 12.39 |
| BC5 | 7.40 | 56.09 | 22.07 | 14.41 |
| BC10 | 4.82 | 56.84 | 24.12 | 14.21 |
| BC20 | 2.66 | 60.11 | 25.33 | 11.85 |
| BC30 | 7.77 | 52.56 | 27.67 | 11.89 |

Mucilage extracted from seeds is composed of carbohydrates, mostly—pectin, cellulose, and hemicelluloses [33]. Regarding the nature of these compounds, high temperature to degrade is usually not required. According to previous articles, structure of mucilage tends to disintegrate at temperature range of 200–300 °C. In this range all three mentioned components of mucilage decompose therefore, in DTG curve single high intensity peak is commonly observed [34]. With a reference to investigations carried out previously, plant seeds mucilage contains divergent amount of ash, depending on plant species as well as extraction conditions. It was acknowledged that mucilage extracted from flaxseeds has relatively low content of ash, varying from approximately 2 to 6% [35]. Therefore, the ash content was comparatively constant evaluating proximate analysis results of activated biochar with different concentrations of the binder.

Thermogravimetric analysis results indicated that formed anodes possessed appropriate thermal stability regardless of binder concentration; activated biochar anodes were thermally stable at the temperature of up to 200 °C.

3.2. Mechanical Resistance

BC10, BC20 and BC30 samples with 10, 20 and 30 wt.% binder concentration respectively were investigated in order to determine the compression strength of anodes. BC5 sample was not examined owing to an insufficient maintenance of cylindrical-shaped anode form in atmospheric pressure. Therefore, it was estimated that in order to implement an anode formation from activated biochar, the concentration of the mucilage binder should be at least 10 wt.%. Dimensions of anodes prepared for the experiment are given in Table 2.

Table 2. Dimensions of activated biochar anodes with 10, 20 and 30 wt.% binder concentrations for compression strength analysis.

| Samples | Diameter, mm | Height, mm | Compression Surface Area, mm ² |
|---------|--------------|------------|---|
| BC10 | 13.04 | 16.21 | 134.58 |
| BC20 | 13.02 | 15.10 | 133.14 |
| BC30 | 13.09 | 15.78 | 133.55 |

The compression deformation experiment showed the mechanical resistance changes when a vertical compressive force is applied in 0.5 mm/min rate. The deformation of samples proceeded relatively uniformly with low compression up to 0.2 mm comparing all three samples. The differentiation started to emerge when applied pressure exceeded 6.7 bar force. With the increase of compression force to 22 bar, deformation of BC10 and BC20 was even and increased constantly reaching 0.8 mm, while BC30 sample required much greater pressure—52 bar to deform at the same dimension.

BC30 sample required the highest pressure to crack at 1.4 mm deformation point—96 bar compared with BC20 and BC10 samples. BC20 sample cracked when maximum compression was equal to 45 bar at 1.43 mm deformation point and BC10—28 bar at 1.2 mm, respectively (Figure 6). Hu et al. [36] performed mechanical resistance experiments of rice husk biochar bound with natural materials of lignin and starch; obtained results showed that the compressive strength was equal to maximum value of 25 and 10 bar respectively. Consequently, a presumption is made that flaxseed mucilage binder is more preferable in terms of higher mechanical resistance provision.

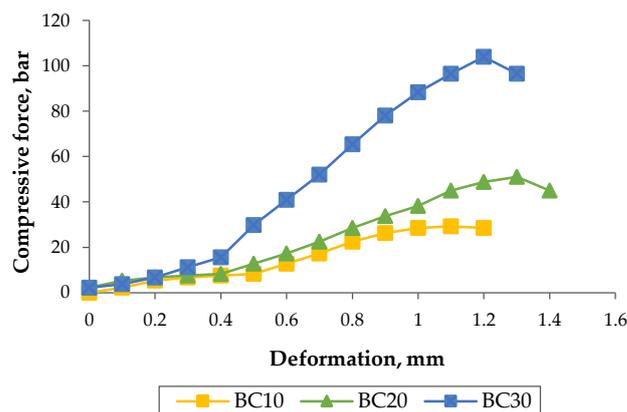


Figure 6. Compression deformation experiment results of biochar anodes with different binder concentrations.

According to results obtained it is concluded that biochar anode with 30 wt.% binder concentration had the highest mechanical resistance and compression strength value of 104 bar. Therefore, considering mechanical strength property, anode with 30 wt.% mucilage binder is the most favourable choice for application in MFC.

3.3. BET Surface Area Analysis

The analysis has revealed a dependency of specific surface area value on the binder concentration in biochar anode. A linear decrease of the specific surface area was observed with the increase of mucilage binder concentration in a sample. This is explained by a blockage of pores occurrence, therefore the higher concentration of the binder tends to block greater number of activated biochar surface pores by means of reducing specific surface area of anode. The mucilage binder reduced specific surface area as following: BC5 specific surface area was equal to 1077.34 m²/g, BC10—1056.49 m²/g, BC20—856.21 m²/g and BC30—796.13 m²/g respectively. Distribution of results is presented in Figure 7.

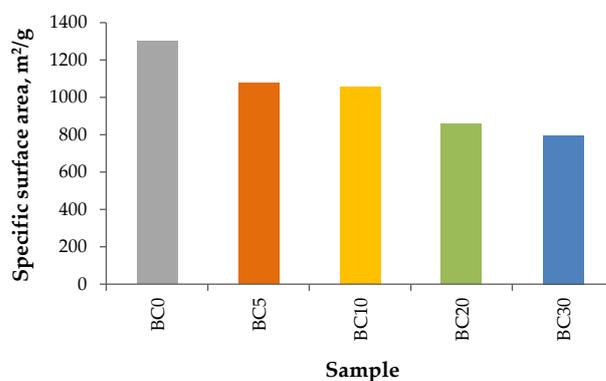


Figure 7. Dependency of binder concentration (wt.%) on the specific surface area of formed anode.

The highest specific surface area was estimated for the binder-free BC0 sample that was equal to 1298.49 m²/g. To compare, Wang et al. [12] carried out the investigation of undefined species algal biochar anodes obtainment by KOH activation technique and determined that such biochar had a specific surface area of 873 m²/g. Zha et al. [10] employed different activation technique by means of soaking eggplant biomass in (K₃[Fe(C₂O₄)₃]·3H₂O) solution prior carbonization and obtained specific surface area of biocarbon equal to 1137 m²/g. On the other hand, utilization of this technique on Rhodophyta seaweed biomass has not provided the result desired. This approach employment on Rhodophyta only provided a specific surface area of 6.2 m²/g of algal de-rived biochar. Therefore, not only the treatment method but the structure and type of biomass plays a vital role to the final result of biocarbon-specific surface area value.

Specific surface area of all investigated samples was competent and sufficient for employment in MFC since the adequate attachment of biocatalysts on the surface of fabricated anodes and biofilm formation would be feasible.

3.4. Electrical Conductivity Estimation

Electrical conductivity is considered as a vital attribute regarding formation of a MFC anode with favourable electron transfer rate value through the electrode. Thus, the determination of electrical conductance of constructed anode is essential. The electrical resistivity value of the sample describes the resistance of electrical current flow through the sample material; therefore the electrical conductivity is described as an opposite dimension to the electrical resistance [37]. The electrical resistivity of BC0, BC5, BC10, BC20 and BC30 samples was measured to determine the electrical conductivity of formed anodes and of bulk-activated carbon comparatively.

Values of measured electrical resistance strongly depended on the pressure applied to the sample. The increase of pressure caused a notable decrease in the resistance value of each sample compressed. This correlation was explained by researchers Sánchez-Gonzalez et al. [38] which elucidated the decline of electrical conductance of carbon material dependency on the pressure increase by the initial sample volume reduction that contributes to the superior compression of the sample.

The initial resistivity values of formed anodes were approximately 30, 46, 112, 159 and 298 Ω for BC0, BC5, BC10, BC20 and BC30 respectively. The influence of applied pressure to average electrical resistance value is illustrated in Figure 8. The clear difference of resistivity values was detected with the compression force applied equal to 5 bar, which impacted resistivity values as following: 0.1; 0.18; 0.19; 0.24 and 0.29 Ω for BC0, BC5, BC10, BC20 and BC30 samples respectively.

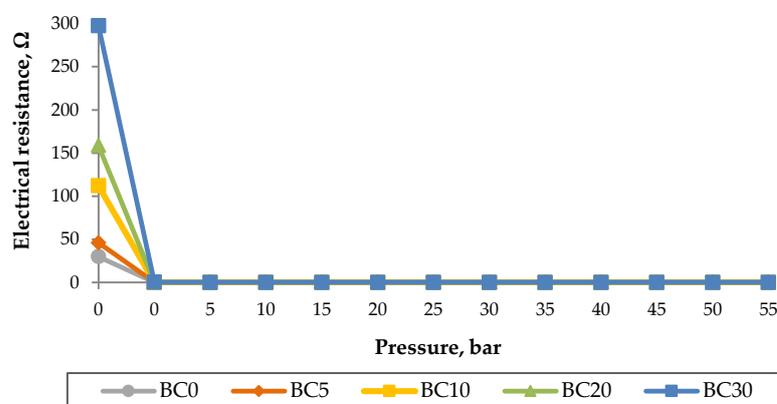


Figure 8. Experimentally measured electrical resistance value (Ω) dependency on the pressure applied to the surface of anode sample.

Results have revealed that the higher proportion of the binder in a sample influenced greater electrical resistance value that was extremely visible with lower pressure applied. El-

evated resistance related to higher concentration of the binder in biochar anode is explained by the limitations of the electrical conductivity of the binding material itself. Previous researches indicated that a solution of mucilage extracted from seeds has a property of hydraulic conductance whereas the electrical conductivity appears due to naturally present electrolytes in mucilage extract dissolved in water [39]. Therefore, the mucilage binder itself gives high resistance values and consequently negatively affects electrical properties of formed electrode.

Figure 9 illustrates considerable changes in average values of calculated electrical conductivity depending on the binder concentration used and pressure applied. Electrical conductivity was calculated firstly determining the impact of samples dimensions to electrical resistivity values obtained experimentally. Initial values of electrical conductivity were particularly low, equal to 0.183, 0.078, 0.055, 0.037 and 0.008 S/m for BC0, BC5, BC10, BC20 and BC30 samples respectively.

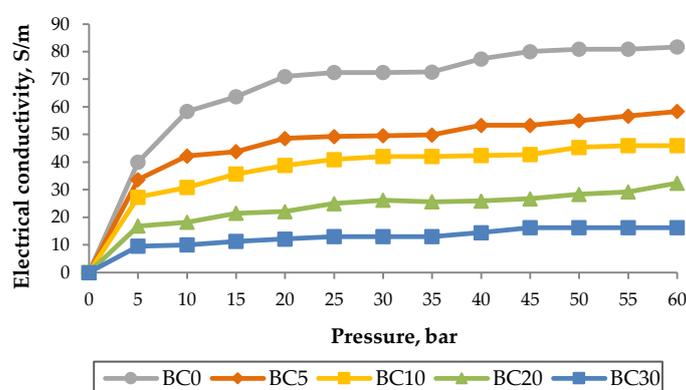


Figure 9. Dependence of calculated electrical conductivity values on the pressure applied to samples with different concentrations of the binder.

The highest electrical conductivity was obtained with bulk biochar BC0 sample that reached a maximum electrical conductivity value of 82 S/m when the pressure applied was equal to 60 bar. Comparatively, Delord et al. [40] investigated binder free carbon nanotube based electrodes and determined that the electrical conductivity of electrodes was equal to approximately 106 S/m. These differences emerge due to the biochar and graphitized carbon structural differences, carbon nanotubes usually is more electrically conductive as it has higher graphitization level compared with a regular biochar [41].

Electrical conductance as opposed to electrical resistance had a tendency to decrease with the elevation of binder content in anode. However, the amplification of applied pressure force conditioned in the increase of electrical conductivity value and the highest conductivity by applying 60 bar compression was achieved as following: 58, 46, 32 and 16 S/m for BC5, BC10, BC20 and BC30 anodes respectively. Therefore, according to the electrical conductivity results it is concluded that biochar anodes bound with 5 or 10 wt.% mucilage binder have the most decent electrical properties required for MFC electrode.

4. Conclusions

This investigation highlighted the potential of a KOH activated seaweed derived biochar employment as an anode material in clean energy generation fulfilment by means of MFC technology. In assistance of flaxseeds mucilage fabricated environmentally friendly anodes possessed different mechanical strength, electrical and surface area properties, whereas good thermal stability was appropriate in all anodes investigated. Evaluation have been made that algal biochar anode with 10 wt.% binding agent had optimum characteristics necessary for electrode along with well maintenance of bound anode form. Higher concentrations of the mucilage binder resulted in the decrease of electrical conductivity value as well as specific surface area reduction which are the very main properties of MFC

electrode; accordingly, biochar anodes with higher content of the binder are considered as not particularly suitable for application in MFC technology. The additional research is required to test whether utilization of constructed algal biochar anodes enables sufficient power density generation in MFC system and feasibility investigation is needed.

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