

Preparation and Study of Acid-Base and Ion-Exchange Properties of Biochar from Waste Coffee Grounds

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ABSTRACT

Increased consumption of coffee in the world leads to the accumulation of food waste that is not properly utilised properly, but have prospects for further processing into a targeted with added value. The aim of this study is to produce biochar from waste coffee grounds by coffee grounds by conventional pyrolysis and microwave irradiation, determination of its chemical and particle size distribution, study of acid-base and ion exchange properties, ability to bind ions and lead ions for further use as an additive in the production of biogas production. Given the high cost of conventional pyrolysis to produce the required volumes of biochar, it is promising to consider an alternative option that will be significantly cost-effective and efficient. After carbonisation, we determined the biopolymer composition, acid-base and ion exchange properties of the raw materials and biochar using various methods, such as the Kjeldahl Hogedron-Jensen, potentiometric titration and others. The results of the maximum cation exchange capacity of raw materials and biochar indicate that biochar has a less pronounced tendency to exchange cations in the range of 0.89–1.15 $\mu\text{eV/g}$ than raw materials, the value of which is mainly in the range of 1–3 $\mu\text{eV/g}$, which shows less influence of biochar on the mineral balance of microorganisms during anaerobic digestion. The values of the anion exchange capacity of biochar are in the range of values 0.7–1.2 $\mu\text{eV/g}$, and the pH value of the acidic groups of biochar lie in the range of 7.1–10.7 (characterising them as weakly acidic groups), pK_a is 9.6–10.7. The curves of potentiometric titration of biochar are determined by the additive contribution of all ionised groups of biochar and allow us to classify the studied products as polyfunctional ion exchangers type ion exchangers. Results of the study of biochars from waste coffee grounds show that they have ampholytic properties and act as acceptors of metal ions, as well as function as a mild pH regulator, which is important in anaerobic digestion of food waste into biogas to increase the yield of the resulting gas in accordance with the biocircular green economy model.

Keywords: biochar, coffee grounds, pyrolysis; microwave irradiation, metal ion acceptors, ampholytes.

INTRODUCTION

The accumulation of food waste (FW) and its inefficient disposal contributes to the acceleration of global warming, which negatively affects the environment, flora and fauna in different regions of our planet. There are many biotechnologies for processing and utilising food waste to reduce its amount and, at the same time, obtain targeted value-added products, for example, biochar, biogas, biodiesel, humus and a number of other

useful products can be obtained from food waste [Chhandama et al., 2022]. One of these technologies is the production of biochar from various food wastes, biochar is a carbon-rich solid material similar to coal, but derived from a different feedstock, namely biomass. This product is an alternative to the already familiar activated carbon and can be used for various processes, such as improving soil and fertility, increasing biogas yields in anaerobic digestion [Ihoeghian et al., 2023; Parthasarathy et al., 2023; García-Prats et

al., 2024]. The biomass for biochar production can be different, such as food waste from hotel and restaurant complexes, agricultural waste, organic fractions from wastewater treatment plants or municipal waste, etc. In the context of this study, it is proposed to use spent coffee grounds (SCG) as a raw material, which is generated in huge quantities due to the increase in coffee consumption worldwide and in Ukraine [International Coffee Organisation, 2023]. The global experience shows an increase in coffee production, for example, during the year, this figure was 9 million tonnes of ground coffee worldwide, of which about 6 million tonnes of used SCG are produced [Campbell et al., 2024]. In 2022, coffee became one of the main food products exported in the world, with a total volume of 8,466 million tonnes, which generates a value of 46,397 million USD [Laos-Espinoza et al., 2024]. This product continues to be actively popularised around the world, with North America being the leader in coffee consumption, followed by Europe, for example, the UK consumes coffee significantly less than other countries in the region, with 2.9 kg of products per capita (approximately 98 million cups per day or 175,000 tonnes per year) [Gosalvitr et al., 2024]. Approximately 650 kg of SCG is produced from 1 tonne of green coffee beans [Kim et al., 2024].

The high content of organic substances (cellulose, hemicellulose, lignin, etc.) in SCG makes this waste a valuable feedstock for bioenergy production, and a number of studies have already confirmed the effectiveness and shown positive results [Pambudi et al., 2024].

Slow pyrolysis is the main thermochemical method used to produce biochar by prolonged decomposition of biomass at high temperature (250–600 °C) with a lack of oxygen and at a low heating rate [Ihoeghian et al., 2023]. Pyrolysis produces three main products (biochar, bio-oil and synthesis gas), the ratios and characteristics of which can be varied depending on the operating parameters and can be further influenced by activation with physical (thermal pyrolysis, microwave irradiation, etc.), chemical (acids, salts and alkalis) or other modification methods (addition of heteroatoms) [Parthasarathy et al., 2023; García-Prats et al., 2024; Amer et al., 2022]. Studies have been conducted to vary the effect of CO₂ atmosphere with N₂ on the slow pyrolysis of food waste, experiments were conducted at different temperatures of 400, 500 and 600 °C with the same heating rate of

5 and 15 °C/min for 1 hour for all samples. The resulting biochar had different physicochemical properties; the CO₂ atmosphere increased the biochar yield, while decreasing the amount of volatile substances, increasing the carbon content, and obtaining lower molar ratios of O/H and O/C compared to the N₂ atmosphere. The pore volume (PV) and surface area (SA) of biochar varied depending on the feedstock used, e.g.: from food waste (FW) SA 19.9140 m²/g and PV 0.0097 cm³/g; from rice husk SA 141.0356 m²/g and PV 0.0843 cm³/g; from grape waste (GW) SA 104.5600 m²/g and PV 0.0661 cm³/g [Premchand et al., 2022].

Many studies have been conducted on biochar for various physicochemical properties, such as high cation exchange capacity (CEC), specific surface area, porosity, various surface functional groups, and high-water holding capacity, and the carbon sequestration potential of 2.57 to 6.60 Gt CO₂ equivalent per year has been estimated on a global scale [Li and Skelly, 2023].

A very wide range of food waste is used for biochar production, depending on the region and climatic zone, which has the potential for further use, such as cassava peel waste, for its transformation into biochar using an upward air flow reactor with retort heating, where carbonisation took place for 160 minutes at a peak temperature of 338 °C. The pyrolysis resulted in a 55.13% increase in biochar yield compared to other feedstocks. This biochar consists of similar, but more oxygen-containing functional groups, the surface area of BET and pore diameter of BJH are 319.784 m²/g and 2.447 nm, respectively, compared to other wastes. This means that cassava peel waste has the potential to be used as a raw material, can be thermochemically processed into biochar in a reactor without electricity, and the process is cheap enough, environmentally friendly, and can have a positive impact on reducing greenhouse gas emissions. Compared to cassava peel biochar, the surface area of BET was lower compared to the literature, where during thermochemical carbonisation, sugarcane bagasse waste was 533.6 m²/g and oil palm waste was 352.9 m²/g [Odeyemi et al., 2023].

The production of biochar from waste coffee grounds is not something new and unexplored, and a number of studies have already shown that its use is cost-effective and efficient for a wide range of processes, for example, in the adsorption of chromium (VI) from wastewater. For this purpose, biochar was obtained by pyrolysis at a temperature and heating time of 400, 600 °C

and 1, 2 h, respectively, and using KOH as an activating agent, which was subsequently used in wastewater treatment with a decrease in the Cr^{6+} content, so that the chromium concentration was reduced from 13 ppm to 0.1 ppm per 1000 m^3 of wastewater. At the same time, the cost of this treatment method is much more favourable than using conventional zeolites (£12.60), namely the use of SCG biosorbent is £0.88, while commercial activated carbon is £0.93. Commercial activated carbon has low adsorption capacity and low removal rates compared to SCG [Campbell R., et al., 2024]. In another study, oxidative torrefaction improved the properties of SCG as a fuel, increasing the HHV with increasing temperature and residence time, the bound carbon, the ignition temperature (T_i) and the burning temperature (T_b), while decreasing the volatile content, moisture, mass and energy yields. For biochar, T_i was between 242.8 °C and 281.4 °C, and T_b was between 570.7 °C and 625.6 °C, and lower ash content was demonstrated compared to coal [Pambudi et al., 2024].

In another study, two samples of biochar from SCG were produced in two ways in a muffle furnace and a tube furnace to compare the efficiency of the carbonisation process, so that the specific surface area of the sample from the muffle furnace was 124.26 m^2/g , which is 37 times higher than that of the other sample from the tube furnace. After varying the conditions, it was determined that the optimal temperature for both furnaces was 55 °C, pH = 4, heating time = 10 hours and concentration – 80 mg/l. The pore size of the muffle furnace sample was significantly larger than that of the tube furnace, namely 3.42 nm and 0.015 nm, respectively [Chen et al., 2024].

Recent studies have demonstrated good results in the effective removal of highly toxic elemental mercury (Hg^0), benzene extraction, and adsorption of copper ions from various aqueous solutions, with various microorganisms (*Bacillus*, *Pseudomonas*, *Azotobacter*, and *Rhizobium*) successfully inoculated using biochar [Li and Skelly, 2023; Parthasarathy et al., 2023]. Biochar is actively used in industrial processes in cosmetics (cleaning agent), medical (activated carbon), food (feed additives), textile (catalytic carriers for wastewater treatment from dyes), construction (insulation of buildings, etc.), electrode manufacturing, for example, biochar is used to remove resins, or as catalysts for synthesis gas purification [Parthasarathy et al., 2023].

Microwave methods for bioenergy production are becoming increasingly popular in recent years, as it is a type of thermochemical conversion of biomass into biochar, but it has its own process features, unlike other types of pyrolysis, it does not require the use of batch furnaces or fixed bed reactors, thermal decomposition occurs by exposure to electromagnetic heating in the absence of oxygen. Another positive factor for the use of microwave irradiation is the faster heating start, heating speed and heating uniformity. Typically, commercially available microwave ovens operate at frequencies of 915 MHz and 2.45 GHz, with a wavelength range of 10–3 and 1 m and a photon energy of 1.2 μeV to 1.2 meV [Allende et al., 2023].

Regardless of the method of biochar production, its properties are influenced by a number of operating parameters of the pyrolysis process, namely temperature, speed, heating time and characteristics of the feedstock.

The aim of the study is to obtain biochar as an additive in the anaerobic digestion of food waste from the hotel and restaurant complex and to characterise its acid-base and ion-exchange properties. To achieve this goal, the following tasks were solved:

1. Production of biochar from waste coffee grounds using traditional pyrolysis and microwave irradiation.
2. Determination of the chemical composition of the obtained biochar.
3. Determination of the granulometric composition of crushed biochar.
4. Study of acid and cation exchange properties of spent coffee grounds and biochar.
5. Investigation of the ability of biochar and waste coffee sludge to bind calcium and lead ions.
6. Investigation of anion exchange properties of biochar.

METHODS AND MATERIALS

Production of biochar by traditional pyrolysis

As a raw material for biochar, we used waste coffee sludge from the Zucchini restaurant (Odesa, Ukraine), which was collected during three working days in the summer season of its operation, and was not separated by the ratio of Arabica/Robusta or by type of coffee roasting. In general, during 1 working day in the summer, a restaurant produces between 1.05 kg and 1.5 kg (approximately

145–180 cups of coffee), while the number of cups of coffee in coffee shops can reach from 1600 to 1800 (for example, to make an espresso drink, about 7 grams of finely ground beans, which make up 1 teaspoon, are required for a single cup of coffee, and 6–8 grams for a cone-type coffee machine). No additional processes to reduce the size of the raw material were reproduced.

The pyrolysis process was carried out in a tubular furnace with continuous purging of nitrogen gas at a rate of 30 ml/min. The heating rate was constant at 15 °C/min. The raw material samples were kept at 300 °C and 500 °C for 15 minutes. The resulting biochars were labelled with heating temperatures as biochar-300 and biochar-500, respectively. The carbonation process was carried out in an experimental laboratory setup, the scheme of which is shown in Figure 1.

The spent coffee grounds 8 (40 g), after washing and drying, are placed in a perforated bottom reaction beaker 7. With the valves 14 and 16 closed, open the valve 15 and purge the installation with nitrogen to remove air from the reactor 5. The electric heater 4 of the reactor 5 is switched on and the process temperature is set using a sensor built into the compensation recorder 11. The temperature is controlled using a thermocouple 10. The generated pyrolysis gas is analysed for component content using a Gasboard 3100R gas analyser 13.

To determine the granular composition of the obtained biochar, after the pyrolysis process in a ball mill, it was crushed using the sieve method, sieved

into different fractions (mesh size 0.1–2.0 mm), and the weight of each fraction was determined. Biochar after carbonisation retains its original morphological shape and has a dark brown color.

Production of biochar by microwave irradiation

During the study, a commercial microwave oven Beko with a microwave power of 800 W was used, where the irradiation process took place for 30 minutes at a temperature of 230 °C (Figure 2). The spent coffee grounds were placed with deionised water in a reactor, which was used as a porcelain bowl, in a weight ratio of raw materials to water of 1:5 and tightly closed.

The microwave irradiation process parameters were set to 230 °C and the exposure time to 30 minutes, and after setting them, the experiment was started by keeping the samples in the reaction mixture for the appropriate time. At the end of the experiment, the reactor was cooled to room temperature using a fan, and the final product was washed with deionised water and dried at 105 °C in an oven for 24 hours. The tests were carried out in triplicate to obtain more accurate data and further analysis. Using the gravimetric method, the biochar yield was determined and expressed as a percentage of biomass, gaseous products (both condensed and non-condensed) were removed from the reactor by gravity through the condenser tube.

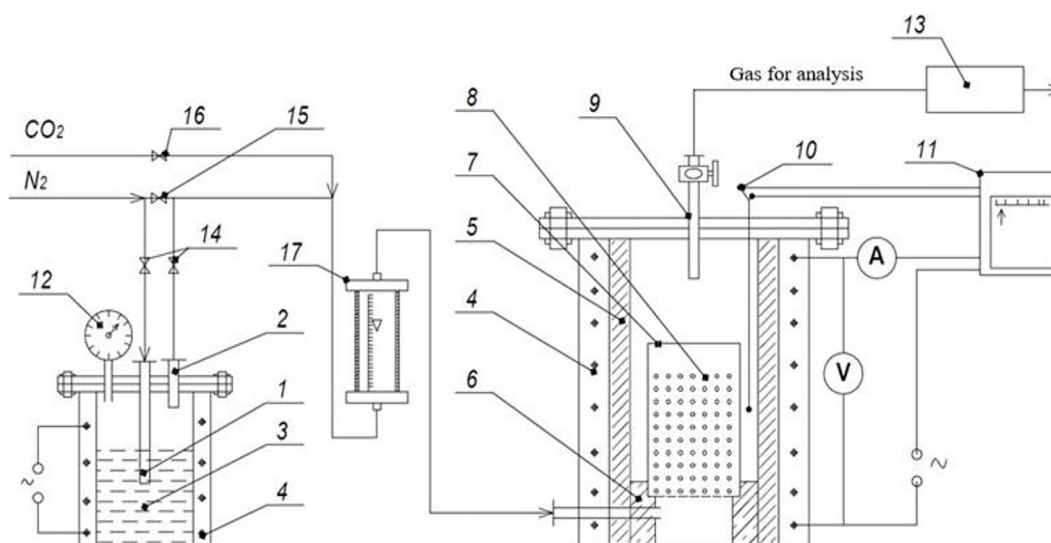


Figure 1. Schematic of the experimental unit for carbonisation of waste coffee grounds: 1 – nitrogen inlet pipe; 2 – nitrogen-water vapour mixture outlet pipe; 3 – steam generator; 4 – electric heater; 5 – reactor; 6 – stop ring; 7 – reaction flask with perforated bottom; 8 – raw material; 9 – gas outlet pipe; 10 – thermocouple; 11 – KS-2 device; 12 – pressure gauge; 13 – gas analyser; 14, 15, 16 – valves; 17 – flow meter



Figure 2. Beko microwave oven with 800 W microwave power

Biopolymer analysis of raw materials and biochar

Nitrogen was determined by the Kjeldahl method [Aoac, 2005; Aguirre, 2022], the factor for the determination of protein substances was 6.00 [Jara et al, 2022]. The content of hemicelluloses in the feedstock and biochar was determined by treating them with HCl with a mass fraction of 2% according to the method of hydrolysis of easily hydrolysed polysaccharides [Krusir et al., 2020]. The Hogedron-Jensen method was used to determine the content of hemicelluloses, followed by multiplying the value by a factor of 0.88 [Pillsbury et al., 1934]. The cellulose content was determined by hydrolysing the residues after the separation of hemicelluloses in the presence of 85% H₂SO₄ for 5 hours at 100 °C [Krusir et al., 2020]. Similar to hemicelluloses, reducing substances were determined in hydrolysates and multiplied by a factor of 0.9. Lignin was determined as the residue after cellulose hydrolysis [Zhang et al., 2024]. Ash was determined by the gravimetric method.

Structural characteristics of feedstock and biochar

The structural characteristics of the feedstock and biochar were determined using a standard vacuum absorption unit with a McBain quartz spring at a temperature of 25 °C [Ioelovich et al., 2022]. Mercury levels were measured using a KM-8 catheter with an accuracy of 0.5%. During the experiments, the unit was enclosed in an organic glass enclosure in which the temperature was maintained at 25 ± 0.2 °C using a specially designed thermostat. The mass of sorbed water was determined by the formula:

$$Q = \frac{\Delta l}{\Delta L \cdot M} \quad (1)$$

where: ΔL – elongation of the quartz helix depending on the mass of the sorbent; Δl is the elongation of the quartz helix depending on the mass of the sorbate; M – molecular weight of the sorbate.

Acid-base and ion-exchange properties of biochar

To study the acid-base and ion-exchange properties of the biochar samples, potentiometric titration using the method of separate weights was used [Ioelovich et al., 2022]. To determine the acid and basic functional groups, they were first reduced to the form of an internal salt. To do this, biochar preparations were pretreated with water until a neutral reaction, which led to the hydrolysis of the corresponding forms (acidic and basic). Further, the obtained biochar samples were titrated with alkalis to determine the basic groups.

The ionic strength of the solutions was maintained constant by adding the calculated amount of electrolyte, KCl, to the solution. The value of the ionic strength is $\mu = 1$. The Henderson-Hasselbach equation [Cherno et al., 1992] was used to calculate the pK value of acid (basic) groups:

$$pK = \overline{pH} + \lg \frac{\lambda}{1-\lambda} \quad (2)$$

where: pK – acid-base dissociation constant; pH - pH value inside the ionite; λ – degree of neutralisation of the solution.

At $\lambda = 0.5$, i.e., in the case of 50% saturation of the ionite with ions, the equation takes the form:

$$\overline{pH} + \lg [Na^+] - \lg \frac{[x]}{2} \quad (3)$$

where: pH – value of this value in solution; $[Na^+]$ - is the concentration of ions in the external solution, meq/g PV; $[x]$ – is the concentration of active groups, mcg/g PV.

Statistical processing of the experimental results was carried out using R, Prism and Excel software.

RESULTS AND DISCUSSION

Food waste is mostly lignocellulosic materials, which include cellulose (a type of glucose polymer with a well-ordered structure and long chains), lignin (monomers of phenolic nature forming branched molecules with long chains, an

important component for gluing cellulose fibres together) and hemicelluloses (branched polysaccharides consisting of two or more monosaccharides) [Cherno et al., 2010]. All organic compounds that make up biomass have certain temperature intervals during the decomposition process during pyrolysis without oxygen, the main parameters affecting the output product are: process temperature, residence time, biomass type and heating rate [Sharma et al., 2015; Cha et al., 2016]. Decomposition of hemicellulose occurs in the temperature range of 220–315 °C, cellulose – 315–400 °C, resulting in non-condensable gas and condensable organic vapours. The process of lignin decomposition is slow, starting at 160 °C and ending at 900 °C [Yaashikaa et al., 2019].

Table 1 shows the results of the study of the chemical composition of raw materials and biochar, namely: biochar obtained by pyrolysis at 300 °C (biochar-300), biochar obtained by pyrolysis at 500 °C (biochar-500) and biochar obtained by microwave irradiation (biochar-MX).

According to the results of determining the chemical composition of raw materials and biochar obtained by pyrolysis and microwave irradiation, the proportion of lignin and ash increases with increasing pyrolysis temperature. The proportion of cellulose in the biopolymer composition of biochar obtained by microwave irradiation also increases.

In order to increase the active surface of the biochar, the material after carbonisation was subjected to grinding in a ball mill with subsequent particle size classification. The particle size study data are shown in Table 2. Table 2 shows that the highest content (83.5% by weight) in carbonitic acid after grinding is characterised by a fraction

of particles with a size of < 0.1 mm. Biochars affect mineral metabolism by changing the pH, which is an important aspect when used as an additive for anaerobic digestion of food waste. This phenomenon is based on the ion-exchange properties of biochars, which are caused by the presence of various ionic groups of both acidic and basic nature. The sources of the former can be hemicellulose, lignin, and protein, which is a component of biochar; being an ampholyte, it also has basic properties due to the presence of a number of R-groups in amino acids.

Some researchers believe that the large mass of biochar used can have a negative impact on the absorption of calcium, iron and some trace elements due to the irreversible binding of the latter by the biochar. Others deny the possibility of mineral imbalance under the influence of biochar, arguing that the main components responsible for binding cations (hemicellulose) are almost completely decomposed by microorganisms, thus releasing these ions and making them available again for the metabolic processes of microorganisms.

Assuming that the evaluation of the ways of biochar influence on anaerobic digestion processes should take into account their ability to function as ion exchangers, we studied their acid-base and ion exchange properties. The biochar was characterised by potentiometric titration. The objects of study were spent coffee grounds, biochar-300, biochar-500 and biochar-MX obtained by microwave irradiation. Typical curves of potentiometric titration of biochar are shown in Figures 3 and 5. Their character is determined by the additive contribution of all ionised groups of biochar and allows us to classify the studied

Table 1. Results of determining the chemical composition of raw materials and biochar samples

Biomass	Protein (%)	Lipids (%)	Hemicellulose (%)	Pulp (%)	Lignin (%)	Ash (%)
Coffee grounds (rawmaterials)	11.2	15.4	19.1	8.6	24.3	1.2
Samples obtained by pyrolysis of raw materials						
Biochar-300	5.6	7.5	10.7	20.3	29.3	6.3
Biochar-500	1.4	2.3	6.7	27.7	31.9	8.9
Samples obtained by microwave irradiation of raw materials						
Biochar-MX	2.7	3.8	8.5	25.2	33.5	6.1

Table 2. Particle size distribution of Biochar-500 after grinding

Particle size, mm	> 1	1–0.61	0.61–0.45	0.45–0.30	0.30–0.25	0.23–0.17	0.17–0.10	< 0.1	Total
Content, %wt.	0.3 ± 0.02	0.1 ± 0.01	0.7 ± 0.05	3.8 ± 0.08	0.1 ± 0.01	6.9 ± 0.1	4.6 ± 0.08	83.5 ± 0.43	100

products as polyfunctional ion exchangers. On the basis of these curves, the concentration of individual ionic groups and their total content in biochar was determined. To do this, the above titration curves were expressed in differential form (Figures 4, 6), which made it possible to determine the location of the titration jump more accurately. The pK values of acid (basic) groups were determined by the Henderson-Hasselbach equation for polyelectrolytes. Below, in Table 3, the values of the maximum cation exchange capacity of these raw materials and biochar are given. Their values indicate that biochars have a less pronounced tendency to exchange cations than raw materials, the cation exchange capacity of which is mainly in the range of 1–3 $\mu\text{eV/g}$. The range of changes in this indicator of biochar is narrower and lies in the region of low values – 0.89–1.15 $\mu\text{eV/g}$. It should be assumed that

the lower value of the cation exchange capacity of biochars corresponds to their lower impact on the mineral balance of microorganisms during anaerobic digestion.

The integral value that characterises the ability of used coffee grounds to exchange cations (anions) depends on the content of individual groups with different degrees of ionisation in the raw material. The local environment has a strong influence on the pK value. Table 3 shows the apparent pK values of different types of ionised groups in biochar and their quantitative contribution to the integral exchange capacity of biochar. It is known that strong acids have low and strong bases have high pK values. According to the data presented here, the pH values of the acidic groups of biochar lie in the range of 7.1–10.7, which characterises them as weakly acidic groups. For comparison, the following data are given: pK_a of acetic

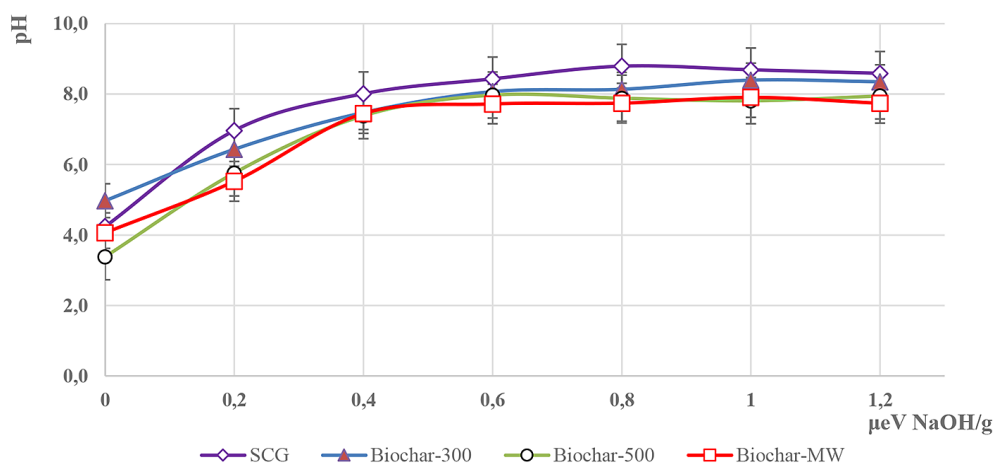


Figure 3. Integral curves of potentiometric titration

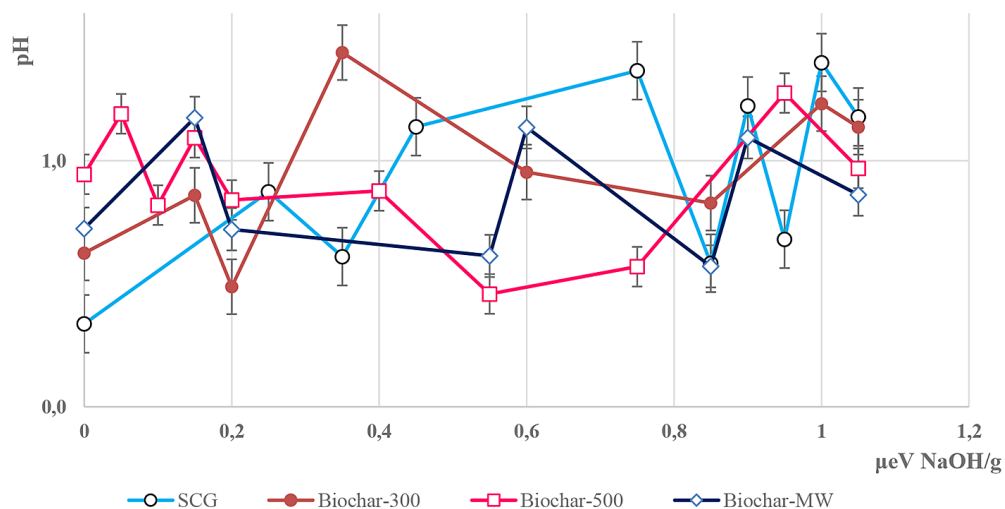


Figure 4. Differential curves for potentiometric titration

acid is 4.76; polyelectrolytes phenolic hydroxyls – pK_a 9–10; sulfhydryl group of cysteine – 8.3; guanidine group of arginine – 12.5. Thus, it is obvious that the assignment of acid groups to biochar, which simultaneously include not only all the substances mentioned in the example, but also other groupings, seems to be very difficult. It is possible only with a large degree of assumption to attribute the biochar groups with the lowest pK_a (7.1–7.5) to carboxyls of uronic acid residues in hemicelluloses; with a value of 8 and higher - to phenolic hydroxyls and R-groups of some amino acid residues of protein. At the same time, a very individual approach should be taken to biochars made using different methods. For example, in biochar-300, the acidic properties are determined by the presence of pK_a 9.6–10.7, which is most likely phenolic hydroxyls. The raw material has approximately the same number of groups with a similar pK value, although this raw material is characterised by a much higher content of polyphenolic components. Below, in Table 4, we present data characterising the ability of biochar to bind

cations of specific metals - calcium and lead. The first of these was chosen because biochar is most often attributed with a negative impact on calcium balance, so a comparison of biochar and raw materials (waste coffee grounds) in terms of this indicator was of particular interest. The amount of lead ion binding of biochar can provide a preliminary assessment of its ability to bind heavy metal ions present in organic waste.

The results of the analysis showed that Ca^{2+} binds to biochar-500 worse than to biochar-300 and biochar obtained by microwave irradiation. This is probably due to the much lower presence of phenolic substances in biochar-500.

The binding of lead ions is higher and, despite the fact that it is less than that of Biochar-500, which is designed to remove heavy metal ions, this factor should be taken into account when assessing the sorption capacity of biochar. The value of the anion exchange capacity of the biochar is in the range of 0.7–1.2 $\mu\text{eV/g}$ (Table 5). The exception is biochar-500, which has very low values of this indicator, which is probably due to the low protein content of the sample.

Table 3. Acid and cation exchange properties of raw materials and biochar

Sample	The pK_a	Functional group content, $\mu\text{eV/g}$	Maximum exchange capacity, $\mu\text{eV/g}$
Coffee grounds	7.1	0.3 ± 0.3	1.0
	8.0	0.3 ± 0.4	
	9.9	0.7 ± 0.9	
	7.3	0.2 ± 0.3	0.9
	9.8	0.7 ± 1.0	
Biochar-MX	7.4	0.1 ± 0.2	1.1
	7.9	0.2 ± 0.2	
	9.2	0.9 ± 1.2	
Biochar-300	8.4	0.1 ± 0.2	0.9
	9.6	0.2 ± 0.3	
	10.7	0.7 ± 0.9	
Biochar-500	7.2	0.2 ± 0.3	1.2
	7.8	0.5 ± 0.7	
	9.4	0.5 ± 0.7	

Table 4. Characterisation of the ability of samples to bind calcium and lead ions

Sample	Sorption of Pb^{2+}		Sorption of Ca^{2+}	
	mg/g	% of initial weight	mg/g	% of initial weight
Coffee grounds	8.6 ± 0.02	21.5 ± 0.28	2.0 ± 0.2	32.5 ± 2.8
Biochar-MX	12.8 ± 0.07	34.5 ± 0.41	0.2 ± 0.1	4.0 ± 3.3
Biochar-300	13.3 ± 0.12	35.7 ± 0.06	1.7 ± 0.1	28.2 ± 4.6
Biochar-500	10.9 ± 0.05	29.2 ± 0.17	0.2 ± 0.1	2.4 ± 0.3

Table 5. Basic and ion-exchange properties of biochar

Sample	The pK_a	Content of groups of basic nature, $\mu\text{eV/g}$	Maximum exchange capacity, $\mu\text{eV/g}$
Coffee grounds	6.0	0.3 ± 0.3	0.8
	4.9	0.6 ± 0.8	
Biochar-300	7.0	0.3 ± 0.4	0.7
	5.2	0.5 ± 0.7	
Biochar-500	7.5	0.1 ± 0.2	0.1
Biochar-MX	7.3	0.4 ± 0.6	1.2
	6.9	0.3 ± 0.4	
	6.3	0.5 ± 0.7	

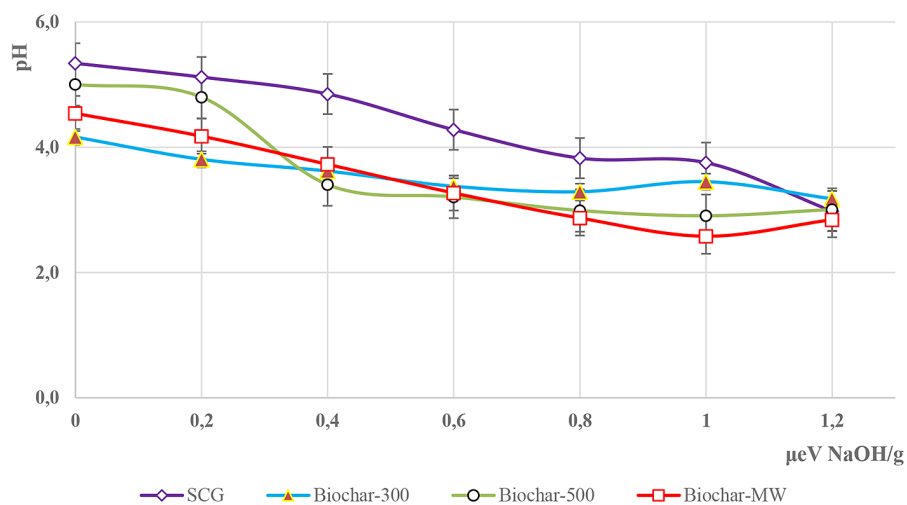


Figure 5. Integral curves of potentiometric titration

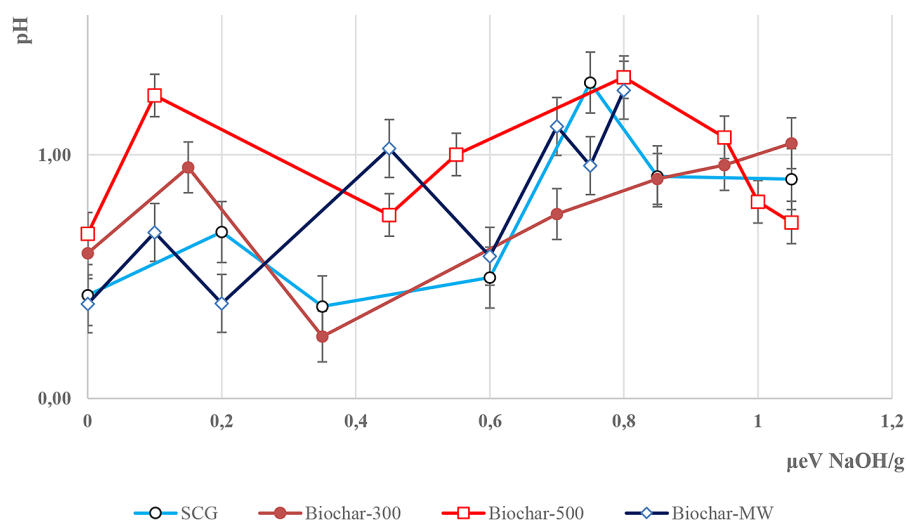


Figure 6. Differential curves for potentiometric titration

The number of tested groups with the ability to exchange anions ranges from 0.1 (biochar-500) to 1.2 (biochar-MX). The groups with the highest pK_a values in the studied biochar range

were found in biochar-500 (pK 7.5), biochar-MX (pK - 7.3) and biochar-300 (pK_b 7.0). Other anion-exchange groups have pK_b from 4.9 to 6.3 $\mu\text{eV/g}$, which characterises them as weakly basic.

The anion-exchange properties of biochar are related to their ability to reduce the acidity of the medium, namely, to increase the pH value during contact with it. This ability of different types of biochar is illustrated by the data shown in Figures 5 and 6. In an alkaline environment, the ion exchange ability of most biochar is more pronounced than in an acidic environment. All biochars have a rather intense effect on the pH value; its maximum change is caused by biochar-MX.

Functioning at a pH of 7–8 as a weak acid, biochars can contribute to an acidic pH change, binding ammonia, which, according to some hypotheses, may be one of the factors contributing to pH changes in anaerobic digestion processes. Based on these data, it can be assumed that Biochar-MX and Biochar-300 will have the most active effect on the pH value. The increase in pH value in contact with raw materials is somewhat higher, the least pronounced is Biochar-500. Thus, possessing the properties of ampholytes, biochars in the process of anaerobic digestion not only act as acceptors of metal ions, but also function as a mild regulator of the pH value.

CONCLUSIONS

In this study, biochar from waste coffee grounds was produced by conventional pyrolysis and microwave irradiation, and their acid-base and ion exchange properties were investigated. The results show that the proportion of lignin and ash increased with increasing temperature during conventional pyrolysis, while the proportion of cellulose increased during microwave irradiation. The results of the study allowed us to classify the investigated products as polyfunctional ion exchangers. At an increased pyrolysis temperature, Ca^{2+} binding deteriorated compared to the biochar obtained by the microwave method. The number of groups tested with the ability to exchange anions ranged from 0.1 (biochar-500) to 1.2 (biochar-MX). In an alkaline environment, the ion exchange capacity of most biochars is stronger than in an acidic environment. All biochars have a rather intensive effect on the pH value, with the maximum change caused by biochar-MX obtained using microwave irradiation, which allows us to predict the possibility and efficiency of its further use in the anaerobic digestion process. Thus, it is possible to predict the effective functioning of

the obtained and studied biochars, which have the properties of ampholytes, act as acceptors of metal ions and are able to function as a soft pH regulator, in the process of anaerobic digestion for the production of biogas from food waste.

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