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**BUCKWHEAT HUSK BIOCHAR: PREPARATION AND STUDY OF ACID-BASE AND ION-EXCHANGE PROPERTIES**Anastasiia O. Tkachenko<sup>1\*</sup>, Olha A. Sahdieieva<sup>1</sup>, Galyna V. Krusir<sup>1,2</sup>, Myroslav S. Malovanyy<sup>3</sup>,  
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**Abstract**

Ukraine is one of the world's leading producers of buckwheat grain, so it is very important to address the issue of including its processing waste in the production cycle. Buckwheat husk is a promising raw material for biochar production. The aim of the study is to obtain biochar as an additive during food waste composting and to characterise its acid-base and ion-exchange properties. The nature of the potentiometric titration curves of biochar is determined by the additive contribution of all ionised groups of biochar and allows us to classify the studied products as ion exchangers of polyfunctional type. It has been shown that, possessing the properties of ampholytes, biochars in the composting process not only act as acceptors of metal ions, but also function as a soft regulator of pH. The number of groups with the ability to exchange anions ranges from 0.1 (biochar-500) to 1.2 (biochar-MX). The groups with the highest pKa values in the range of biochars studied were found in biochar-500 (pK 7.5), biochar-MX (pK – 7.3) and biochar-300 (pKb 7.0). Other anion-exchange groups have pKb from 4.9 to 6.3 meq/g, which characterises them as weakly basic.

*Keywords:* buckwheat husk; biochar; pyrolysis; microwave irradiation; thermochemical conversion; acid-base properties; ion exchange properties.

**ОТРИМАННЯ ТА ДОСЛІДЖЕННЯ КИСЛОТНО-ОСНОВНИХ ТА ІОНООБМІННИХ ВЛАСТИВОСТЕЙ БІОЧАРУ З ГРЕЧАНОГО ЛУШПИННЯ**Анастасія О. Ткаченко<sup>1</sup>, Ольга А. Сагдєєва<sup>1</sup>, Галина В. Крусір<sup>1,2</sup>, Мирослав С. Мальований<sup>3</sup>,  
Антоніна В. Вітюк<sup>1</sup><sup>1</sup>Одеський національний технологічний університет, вул. Канатна, 112, Одеса, Україна, 65039<sup>2</sup>Інститут екопідприємництва, Школа наук про життя, Університет прикладних наук і мистецтв Північно-Західної  
Швейцарії, Хофакерштрассе, 30, 4132, Муттенц, Швейцарія<sup>3</sup>Національний університет «Львівська політехніка», вул. Степана Бандери, 12, Львів, Україна, 79000**Анотація**

Україна є одним із лідерів виробництва гречаного зерна у світі, тому вирішення питання включення відходів його переробки в виробничий цикл є дуже нагальним. Гречане лушпиння є перспективною сировиною для одержання біоچارу. Метою дослідження є отримання біоچارу як добавки під час компостування харчових відходів і характеристика їх кислотно-основних та іонообмінних властивостей. Характер кривих потенціометричного титрування біоچارу визначається адитивним внеском усіх іонізованих груп біоچارу і дає змогу віднести досліджувані продукти до категорії іонообмінників поліфункціонального типу. Показано, що, маючи властивості амфолітів, біочари в процесі компостування не тільки виконують роль акцепторів іонів металів, але і функціонують як м'який регулятор величини рН. Кількість груп, що мають здатність до обміну аніонів, коливається від 0.1 (біоچار-500) до 1.2 (біоچار-МХ). Групи з найбільшими величинами значень рКа в ряду біоچارів, що досліджувалися, виявлені в біоچارі-500 (рК 7.5), біоچارі-МХ (рК – 7.3) і в біоچارі-300 (рКb 7.0). Інші аніонообмінні групи мають рКb від 4.9 до 6.3 мекв/г, що характеризує їх як слабкоосновні.

*Ключові слова:* гречане лушпиння; біоچار; піроліз; мікрохвильове опромінення; термохімічна конверсія; кислотно-основні властивості; іонообмінні властивості.

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## Introduction

Population growth on the planet leads to an increase in food production, including crop production, thus leading to a rise in the amount of waste from processing plant raw materials in food production.

Buckwheat is an annual pseudo-cereal crop of the genus *Fagopyrum* of the family *Polygonaceae*. The most common species cultivated worldwide are common buckwheat (*Fagopyrum esculentum*) and Tartary buckwheat (*Fagopyrum tataricum*) [1]. In recent years, China, Ukraine, Kazakhstan, the US, Brazil, and Japan have been the leaders in the production of buckwheat grain and its processed products [2]. The popularity of this plant is growing due to the high nutritional value of its grains, which contain numerous nutrients, and antioxidants and are rich in vitamins, especially B. The amino acid composition of buckwheat proteins is well-balanced and has a high biological value. In addition, buckwheat grains are a source of macro- and microelements important for human health, such as Zn, Mn, Cu, Se, K, Na, Ca, and Mg. The high content of rutin, catechins, and some other polyphenols, fiber, and soluble dietary fiber allows buckwheat to be used in the prevention of obesity and diabetes. Recently, studies have also been conducted on the properties of buckwheat's antioxidant components, which confirm its preventive effect against cancer and cardiovascular diseases, as well as its anti-inflammatory and antibacterial effects; the same components can also be used to develop antiviral drugs against COVID-19 [3; 4].

However, the increase in buckwheat cultivation leads to a significant amount of waste. The technological processing of whole buckwheat grain begins with the hulling process, after which the cleaned grains are produced along with the first type of waste, husks, which account for 5 % of the raw material. The cleaned grain can be prepared for milling for the further production of buckwheat flour, after which a new type of waste is formed – bran, which makes up 15 % of the raw material [5]. Buckwheat processing thus produces by-products such as leaves, stalks, hulls, and bran, which are often considered waste. Usually, the inedible parts of buckwheat are disposed of by burning or storing them, which leads to pollution of the air or soil where the waste is stored.

Buckwheat waste, namely buckwheat hulls, can be recycled as a value-added product – biochar. Biochar is a high-carbon product obtained by thermochemical or mechanochemical conversion of carbon-containing materials in an oxygen-free

or limited-oxygen environment from materials such as organic waste, bio-waste, plastics, agricultural waste (manure, dung), food waste, etc. In addition, the pyrolysis of biomass produces several volatile components ( $H_2$ ,  $CH_4$ ,  $CO$ ,  $H_2O$ , etc.), the aggregate of which is called synthesis gas, which can also be separately extracted and used for energy needs [6]. The unique properties of biochar, such as its large surface area, high porosity, functional groups, and high cation exchange capacity, make it very promising for a variety of applications, such as agriculture [7], removal of heavy metals from wastewater (e.g.  $Cr(VI)$  [8],  $Hg(II)$  [9],  $Cu(II)$  and  $Sb(III)$  [10]), removal of organic pollutants [6], catalytic activity [11], reduction of  $CO_2$  emissions [6], etc. Several studies have been conducted on the production of biochar from numerous agricultural wastes, including rice straw and husks [12; 13], wood [14], peanut shells [15], coconut [16], sugar cane pulp [17], wheat waste [18], coffee grounds [19], bamboo [20], etc.

There is a wide variety of biochar production methods, and they all differ in terms of temperature and time spent in the reactor. Among the well-known methods of biochar synthesis are pyrolysis (fast (300–700 °C) and moderate (500–1000 °C), gasification (750–900 °C), hydrothermal carbonation (180–300 °C), flash carbonation (300–600 °C), torrefaction (200–300 °C), microwave pyrolysis, etc. It should also be noted that since thermochemical conversion also produces synthesis gas and bio-oil in addition to biochar, some of the above methods may be more efficient in producing biogas and bio-oil. For example, the study [21], found that fast pyrolysis produces 75 % of bio-oil, while biochar yields only 12 %; gasification produces 85 % of synthesis gas, while biochar is only 10 % [22].

The type of raw material used to produce biochar plays an important role in determining its properties. Cellulose and hemicellulose contribute to the formation of bio-oil, while lignin contributes to the formation of a high yield of biochar [23]. The amount of these compounds in the feedstock determines the chemical, physical, and structural changes in the biochar during pyrolysis [24]. As a result of pyrolysis, micromolecular organic compounds are destroyed, creating voids in the biochar matrix and increasing the total surface area and pore size. In general, biochar produced from lignin-rich biomass has a macroporous structure with a large surface area, high aromatic organic compounds, and low ash content, while biochar from high-cellulosic biomass has a

microporous structure [25]. Another important factor affecting the quality of the biochar is the exposure time, as excessively prolonged pyrolysis can cause melting, shrinkage, and rearrangement of the elements, resulting in a decrease in the surface area and pore size, which in turn will lead to a decrease in the adsorption capacity of the biochar [26]. The chemical composition of the surface affects the behavior of the biochar in different environments, for example, hydrophilic functions in acidic environments and hydrophobic functions in basic environments [27]. Pyrolysis leads to oxygen saturation of the biochar surface and the formation of inorganic functional groups, leading to increased cation exchange properties. It has also been reported that biochar produced by slow pyrolysis has an increased cation exchange capacity [28].

Buckwheat husks are composed mainly of moisture, cellulose, hemicellulose, and lignin. A study [29] showed that buckwheat hulls have a higher fibre content compared to whole grains and bran. Dziedzic K. et al. analysed the fractional composition of dietary fibres and found that the lignin content in buckwheat hulls is 31.60 % per 100 g, cellulose – 35.55 %, and hemicellulose – 14.4 %, which is an order of magnitude higher than in grain and bran. This study also noted the significant sorption capacity of buckwheat products. Studies [30] also confirm the high content of the above fractions of dietary fibre in buckwheat hulls. All of this makes it possible to conclude that buckwheat hulls are promising as a raw material to produce biochar.

One of the many applications of biochar is the possibility of adding it to composts containing various types of food waste. Biochar has many properties that can improve the processes in the compost. Biochar, due to its surface area and porosity, promotes gas exchange and O<sub>2</sub> supply to the inner layers of the compost, which leads to inhibition of the growth of anaerobic microorganisms and, on the contrary, promotes the growth of microorganisms that support the decomposition of organic matter [31]. Biochar is also effective in maintaining the optimum pH [32], helps to restore the C/N ratio [33], prolongs the thermophilic phase [34], retains nitrogen in the compost due to its sorption capacity, prevents its emission [35], and modifies microbial communities [36].

The aim of the study is to produce biochar that can be used as an additive to compost from food and agricultural waste and to characterise its acid-

base and ion-exchange properties. To achieve this goal, the following tasks were performed:

1. Biochar was obtained by conventional pyrolysis and microwave irradiation.
2. The chemical composition of the obtained biochar was determined.
3. The particle size distribution of biochar after grinding was determined.
4. The acid and cation exchange properties of buckwheat hulls and biochar were investigated.
5. The property of biochar and buckwheat husk to bind calcium and lead ions was investigated.
6. The anion-exchange properties of biochar were investigated.

## **Experimental**

### *Biochar production by traditional pyrolysis*

The biochar was made from buckwheat hulls supplied by a Ukrainian processing plant. Due to the small size of the husk ( $\leq 7$  mm), it was decided to leave it in its original size without grinding it beforehand.

The pyrolysis process was carried out in a tubular furnace with continuous purging with 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 one hour. The resulting biochar samples were marked with heating temperatures as T300 and T500, respectively.

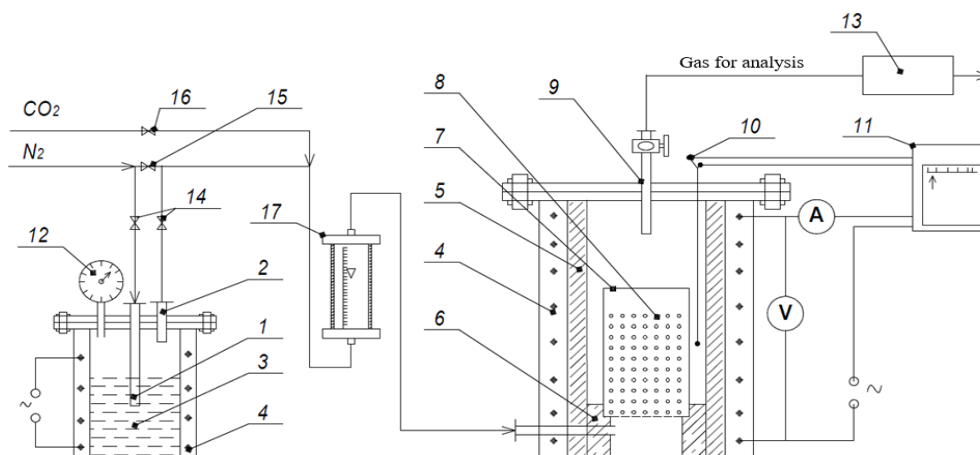
The carbonation process was carried out in an experimental laboratory setup, the scheme of which is shown in Fig. 1.

After washing and drying, buckwheat husks 8 (40 g) are placed in a perforated bottom reaction beaker 7. With valves 14 and 16 closed, valve 15 is opened and the plant is purged with nitrogen to remove air from 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 monitored by a thermocouple 10. The resulting pyrolysis gas is analysed for its component content using a Gasboard 3100R 13 gas analyser.

After pyrolysis, the biochar was collected, crushed and sieved through sieves with a mesh size of 0.1 to 2.0 mm. The resulting carbonised product has a dark brown colour and retains its original morphological shape.

### *Preparation of biochar by microwave pyrolysis*

The experimental setup consists of a conventional Beko microwave oven with a microwave power of 800 W, in which pyrolysis took place for 30 minutes (Fig. 2).



**Fig. 1. Schematic of the experimental unit for buckwheat husk carbonisation: 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**

A microwave oven with a maximum power of 800 W and a temperature of 230 °C was used to conduct the biochar experiment. Deionised water and buckwheat husk were placed in a porcelain bowl (reactor) at the desired ratio of raw materials to water of 1 : 5, and then the reactor was tightly closed. The parameters of the experiment process were set (temperature – 230 °C, holding time – 30 minutes), and then the samples were kept in the reaction mixture for the appropriate time. After completion of the reaction, the reactor was cooled to room temperature with a fan. The final hydrocarbon product (biochar) was washed several times with deionised water and then dried at 105 °C in an oven for 24 hours. After carbonisation, the material was subjected to grinding in a ball mill, followed by particle size classification.



**Fig. 2 - Beko microwave oven**

All experiments and performance analyses were carried out in triplicate.

The biochar yield was determined by gravimetry and expressed as a percentage of ash-free biomass (%).

All gaseous products (both condensed and non-condensed) were removed from the reactor by gravity through the condenser tube.

*Biopolymer analysis of raw materials and biochar*

Nitrogen was determined by Kjeldahl's method [37], the factor for the determination of protein substances was 6.00 [38]. Pectin substances were determined by the spectrophotometric method [39].

The hemicellulose content 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 [40]. The Hogedron-Jensen method was used to determine the hemicellulose content, followed by multiplying the value by a factor of 0.88 [41].

The cellulose content was determined by hydrolysing the residues after hemicellulose extraction in the presence of 85 % H<sub>2</sub>SO<sub>4</sub> for 5 hours at 10 0°C [40]. Similarly to hemicellulose, reducing agents were determined in hydrolysates and multiplied by a factor of 0.9.

Lignin was determined in the residue after cellulose hydrolysis.

*Acid-base and ion-exchange properties of biochar*

To study the acid-base and ion-exchange properties of biochar samples, potentiometric titration using the method of separate weights was used [42]. To determine the acid and basic functional groups, they were first reduced to the form of an internal salt. For this purpose, biochar preparations were pre-treated with water to a neutral reaction, which led to the hydrolysis of the respective forms (acidic and basic). Further, the

obtained biochar samples were titrated with alkalis to determine the groups of basic nature.

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 was used to calculate the pK value of acid (basic) groups [44]:

$$pK = \overline{pH} + lg \frac{\lambda}{1-\lambda},$$

where pK is the acid-base dissociation constant; pH is the pH value inside the ionite;  $\lambda$  is the 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:

$$pK = \overline{pH} + lg \frac{[Na^+]}{[x]},$$

where pH is the value of this value in solution;  $Na^+$  is the concentration of ions in the external solution, mEq/g biochar;  $[x]$  is the concentration of active groups, mEq/g biochar.

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

## Results and discussion

The majority of food processing waste is lignocellulosic material, consisting of cellulose, hemicellulose and lignin. Cellulose is a type of

glucose polymer organised into long chains and has a well-ordered structure. Hemicelluloses are branched polysaccharides composed of two or more monosaccharides. The lignin component consists of phenolic monomers that combine to form branched molecules with long chains. It serves as a binder for gluing cellulose fibres together [45].

The organic compounds present in biomass decompose at a certain temperature in an environment with limited oxygen. Factors affecting pyrolysis products include process temperature, residence time, biomass type, and heating rate [46; 47]. Initially, hemicelluloses decompose at 220 °C, with decomposition being largely completed at 315 °C. Cellulose begins to decompose at temperatures above 315 °C and by 400 °C all the cellulose is converted to non-condensable gas and condensable organic vapours. Lignin begins to decompose at 160 °C, but the process is slow, and decomposition continues until it reaches a temperature of 900 °C [48].

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-MW).

Table 1

Results of determining the chemical composition of raw materials and biochar samples

Biomass	Protein, %	Pectin, %	Hemicellulose, %	Cellulose, %	Lignin, %	Ash, %
Buckwheat husk	4.8 ± 0.1	3.1 ± 0.1	15.5 ± 0.2	27.4 ± 0.1	36.3 ± 0.1	3.6 ± 0.1
Samples produced by traditional pyrolysis						
Biochar-300	1.5 ± 0.2	1.7 ± 0.2	7.8 ± 0.2	31.7 ± 0.2	41.9 ± 0.1	5.6 ± 0.2
Biochar-500	-	0.8 ± 0.1	1.5 ± 0.2	29.1 ± 0.2	50.8 ± 0.2	7.1 ± 0.1
Samples produced by microwave pyrolysis						
Biochar-MW	0.5 ± 0.1	2.1 ± 0.1	10.5 ± 0.1	32.4 ± 0.1	40.3 ± 0.1	3.8 ± 0.1

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 share of cellulose in the biopolymer

composition of biochar produced using microwave irradiation is also increasing.

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 data are shown in Table 2.

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	0.25 - 0.17	0.17 - 0.10	< 0.1	Total
Content, % wt.	0.4 ± 0.04	0.5 ± 0.07	0.8 ± 0.18	2.4 ± 0.01	0.7 ± 0.03	6.9 ± 0.1	5.3 ± 0.06	82.9 ± 0.23	100

Table 2 shows that the highest content (82.9 % by weight) in biochar after grinding is characterised by a fraction of particles with a size of < 0.1 mm.

One of the most important aspects of biochar's impact on organic waste composting processes is its effect on mineral metabolism and ability to change the pH value. This phenomenon is based

on the ion-exchange properties of biochar, which are due to the presence of various ionogenic groups, both acidic and basic. The sources of the former can be pectin, hemicellulose, lignin, and protein, which is a component of biochar, and being an ampholyte, has basic properties due to the presence of several 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 and pectin) are almost completely decomposed by microorganisms, thus releasing these ions and making them available again for the metabolic processes of microorganisms.

If the assessment of the ways in which biochar can influence composting, processes should consider their ability to function as ion exchangers, we studied their acid-base and ion exchange properties. The biochar was characterized by potentiometric titration. Buckwheat hulls, biochar-300, biochar-500 and biochar-MW obtained by microwave irradiation were used as objects of study.

Typical potentiometric titration curves for biochar are shown in Figs. 3 and 5. Their nature is determined by the additive contribution of all ionised groups of biochar and makes it possible to classify the studied products as polyfunctional ion exchangers. These curves were used to determine the concentration of individual ionic groups and

their total content in the biochar. For this purpose, the above titration curves were expressed in differential form (Figs. 4 and 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. Table 3 below shows the values of the maximum cation exchange capacity of these raw materials and biochar. Their values indicate that biochar have a less pronounced tendency to exchange cations than raw materials whose cation exchange capacity is mainly in the range of 1...3 mEq/g. The range of changes in this indicator of biochar is narrower and lies in the low range of 0.89...1.15 mEq/g. It should be assumed that the lower value of the cation exchange capacity of biochar corresponds to their lower impact on the mineral balance of microorganisms during composting.

The integral value that characterizes the ability of buckwheat hulls to exchange cations (anions) depends on the content of individual groups with different degrees of ionization in the raw material. The local environment has a strong influence on the value of pK. Table 3 shows the apparent pK<sub>a</sub> values of different types of ionised groups of 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<sub>a</sub> values of the acidic groups of biochar lie in the range of 7.1...10.7, which characterises them as weakly acidic groups.

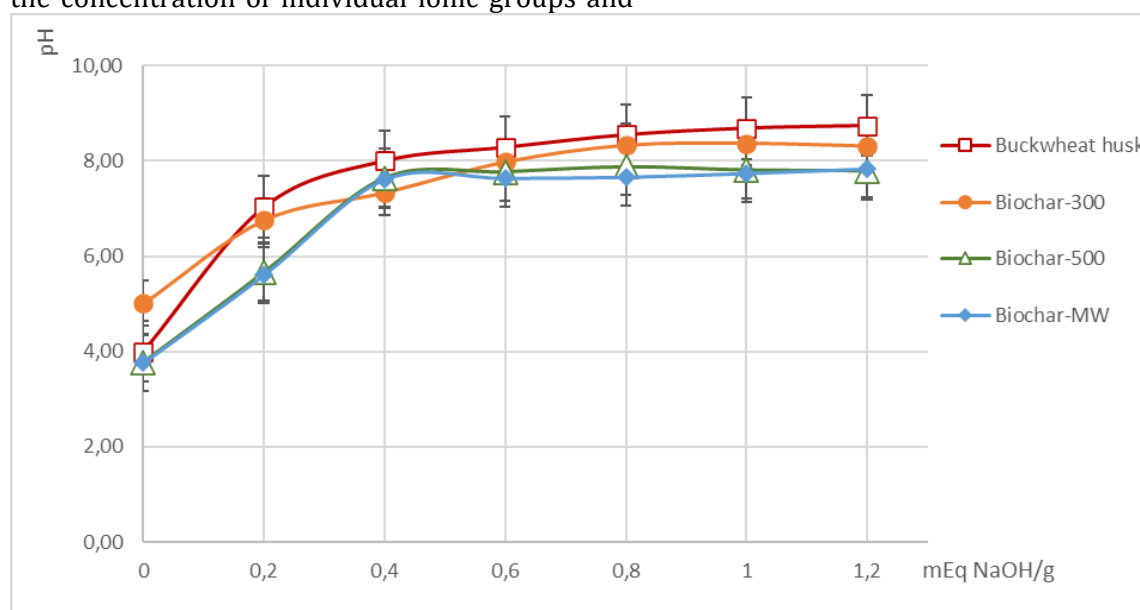


Fig. 3. Integral curves of potentiometric titration

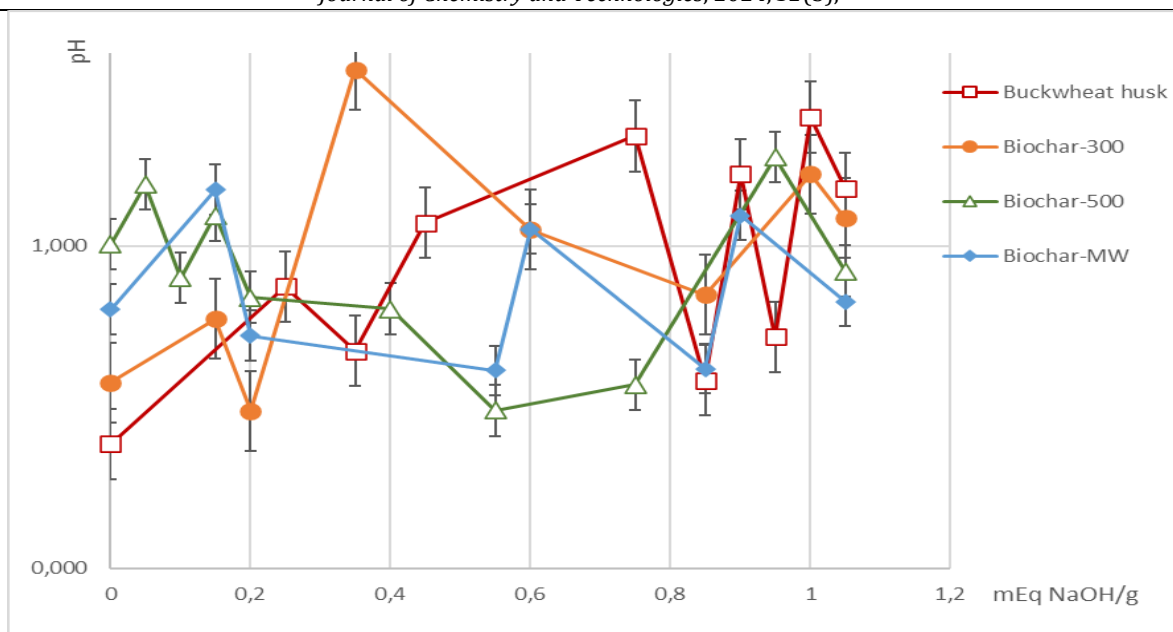


Fig. 4. Differential curves for potentiometric titration

For comparison, the following data are given pH of acetic acid is 4.76; a typical polyelectrolyte pectin has a pH of 3...5; phenolic hydroxyls - 9...10; sulfhydryl group of cysteine - 8.3; guanidine group of arginine - 12.5. Thus, it is obvious that the classification of the acid groups of biochar, which simultaneously include not only all the substances mentioned in the example, but also other groupings, seems to be very difficult. The biochar groups with the lowest  $pK_a$  values (7.1...7.5) can only be attributed with a greater degree of assumption to carboxyls of uronic acid residues in pectin and hemicellulose; those with a value of 8

and higher are phenolic hydroxyls and R-groups of some amino acid residues of protein. At the same time, you should take a very individual approach to bio charms 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 due to phenolic hydroxyls. The raw material has approximately the same number of groups with similar  $pK_a$  values, although this raw material is characterised by a much higher content of the polyphenolic component.

Table 3

Acid and cation exchange properties of raw materials and biochar

Sample	$pK_a$ value	Functional group content, mEq/g	Maximum exchange capacity, mEq/g
Buckwheat husk	7.1	$0.2 \pm 0.3$	1.0
	8.0	$0.2 \pm 0.3$	
	9.9	$0.6 \pm 0.9$	
	7.3	$0.2 \pm 0.3$	
Biochar-MW	9.8	$0.7 \pm 0.9$	0.9
	7.4	$0.1 \pm 0.1$	
	7.9	$0.1 \pm 0.2$	
Biochar-300	9.2	$0.9 \pm 1.2$	1.1
	8.4	$0.1 \pm 0.2$	
	9.6	$0.2 \pm 0.3$	
Biochar-500	10.7	$0.6 \pm 0.9$	0.9
	7.2	$0.2 \pm 0.3$	
	7.8	$0.5 \pm 0.7$	
	9.4	$0.5 \pm 0.7$	1.2

Below, in Table 4, we present data characterizing the ability of biochar to bind cations of specific metals, such as calcium and lead. The choice of the first one is because biochar is most often blamed for a negative impact on calcium balance, so the comparison of biochar and

raw materials (buckwheat hulls) in terms of this indicator was of particular interest. Based on the amount of lead ion binding, biochar can provide a preliminary assessment of its ability to bind heavy metal ions present in organic waste.

Characterization of the ability of samples to bind calcium and lead ions

Sample	Pb <sup>2+</sup> sorption		Ca <sup>2+</sup> sorption	
	mg/g	% of initial wt.	mg/g	% of initial wt.
Buckwheat husk	21.5 ± 0.4	57.8 ± 1.1	2.0 ± 0.2	35.1 ± 4.5
Biochar-MW	18.6 ± 0.3	50.0 ± 0.9	0.2 ± 0.2	4.2 ± 3.8
Biochar-300	21.1 ± 0.4	56.7 ± 1.1	1.6 ± 0.3	29.2 ± 4.6
Biochar-500	7.1 ± 0.5	19.0 ± 1.3	0.1 ± 0.1	2.4 ± 1.6

The results of the analysis showed that Ca<sup>2+</sup> binding by biochar-500 is worse than by 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 even though it is less than that of Biochar-500, which is designed to remove heavy metal ions, this factor should be considered 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 mEq/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.

The number of groups tested that could exchange anions ranges from 0.1 (biochar-500) to 1.2 (biochar-MW).

The groups with the highest pK<sub>a</sub> values in the studied biochar series were found in biochar-500 (pK 7.5), biochar-MW (pK - 7.3) and biochar-300 (pK<sub>b</sub> 7.0). Other anion-exchange groups have a pK<sub>b</sub> of 4.9 to 6.3 mEq/g, which characterises them as weakly basic.

Table 5

Base and ion-exchange properties of biochar

Sample	pK <sub>a</sub> value	Base group content, mEq/g	Maximum exchange capacity, mEq/g
Buckwheat husk	6.0	0.2 ± 0.3	0.8
Biochar-300	4.9	0.6 ± 0.8	
Biochar-500	7.0	0.2 ± 0.3	0.7
Biochar-MW	5.2	0.5 ± 0.7	
Biochar-500	7.5	0.1 ± 0.2	0.1
Biochar-MW	7.3	0.4 ± 0.6	
Biochar-300	6.9	0.3 ± 0.4	
Biochar-500	6.3	0.5 ± 0.7	1.2

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 biochar of different types is illustrated by the data shown in Figs. 5 and

6. In alkaline environments, the ion-exchange capacity of most biochar is more pronounced than in acidic environments. All biochars have a rather intense effect on the pH value; the maximum change is caused by the biochar-MW.

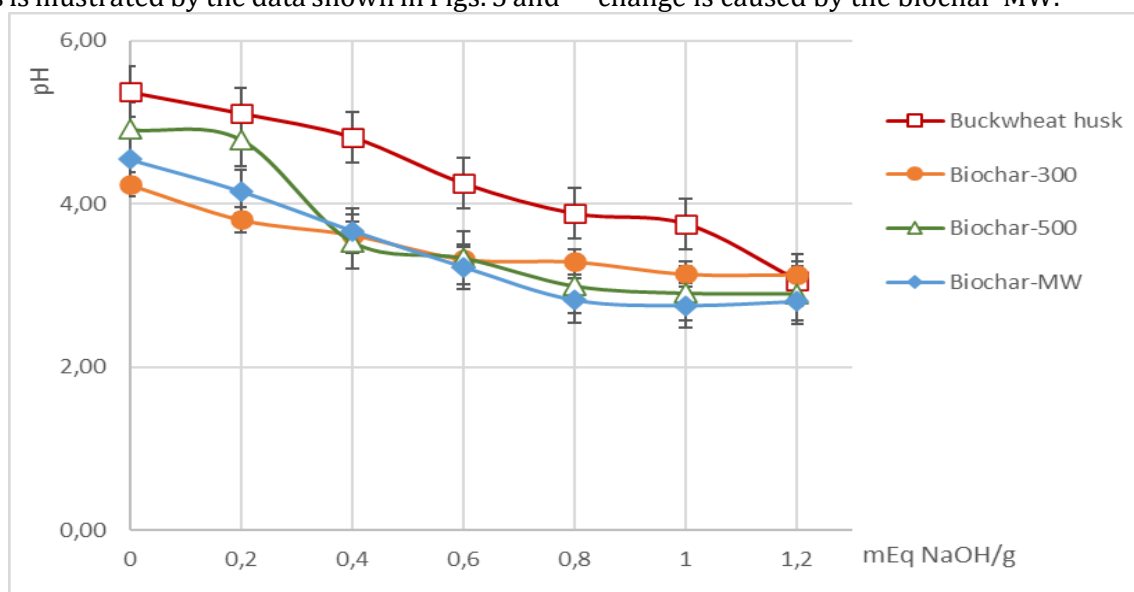


Fig. 5. Integral curves of potentiometric titration



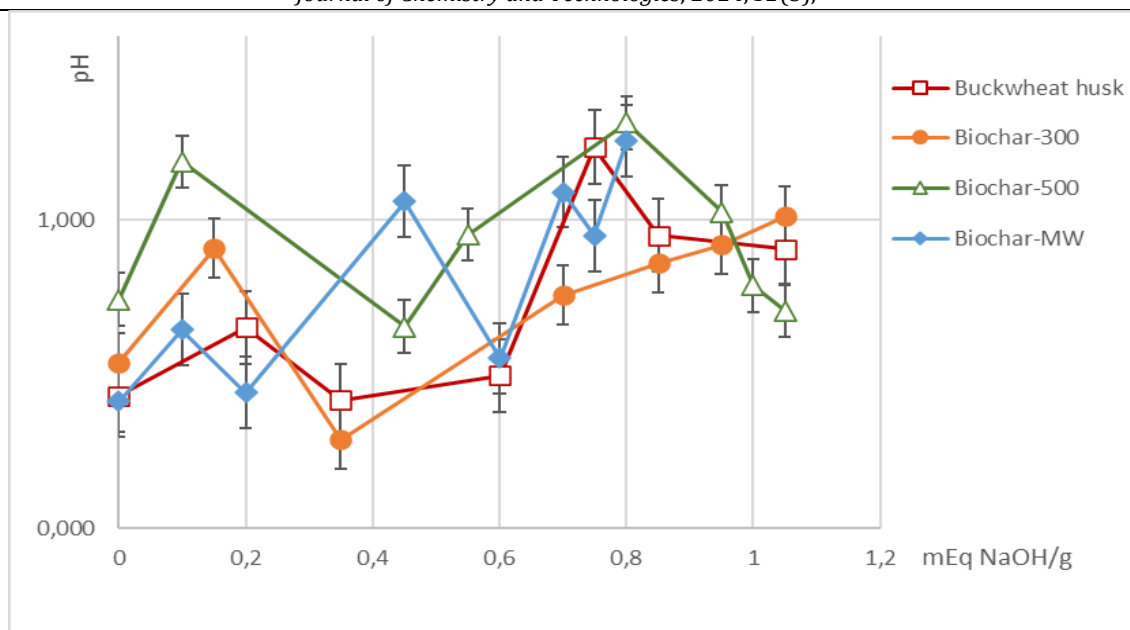


Fig. 6. Differential curves for potentiometric titration

Functioning at a pH of 7...8 as a weak acid, biochar can contribute to an acidic pH change, binding ammonia, which, according to some hypotheses, may be one of the factors contributing to the pH change in composting processes.

Based on these data, it can be assumed that Biochar-MW 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, biochar not only acts as acceptors of metal ions during the composting process, but also function as a soft regulator of the pH value.

### Conclusion

The results of determining the chemical composition of raw materials and biochar obtained by pyrolysis and microwave irradiation show that 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.

The highest content (82.9 % by weight) in carbonized product after grinding is characterized by a fraction of particles with a size of < 0.1 mm.

The appearance of the potentiometric titration curves of biochar is determined by the additive contribution of all ionised groups of biochar and allows us to classify the studied products as ion exchangers of polyfunctional type. The values of the maximum cation exchange capacity of raw materials and biochar indicate that biochar has a less pronounced tendency to exchange cations than raw materials, the cation exchange capacity

of which is mainly in the range of 1...3 mEq/g. The range of changes in this indicator of biochar is narrower and lies in the region of low values - 0.89...1.15 mEq/g. It should be assumed that the lower value of the cation exchange capacity of biochar corresponds to their lower impact on the mineral balance of microorganisms during composting.

The  $pH_a$  values of the acidic groups of biochar lie in the range of 7.1...10.7, which characterizes them as weakly acidic groups.

A very individual approach should be taken to biochar 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 due to phenolic hydroxyls. The raw material has approximately the same number of groups with a similar  $pK_a$  value, although this raw material is characterized by a much higher content of polyphenolic components.

$Ca^{2+}$  binding by biochar-500 is worse than by 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 even though it is less than that of Biochar-500, which is designed to remove heavy metal ions, this factor should be considered when assessing the sorption capacity of biochar.

The value of the anion exchange capacity of biochar is in the range of 0.7...1.2 mEq/g. The exception is biochar-500, which has very low values of this indicator, which is probably due to the low protein content in the sample.

The number of tested groups with the ability to exchange anions ranges from 0.1 (biochar-500) to 1.2 (biochar-MW). The groups with the highest  $pK_a$  values in the studied biochar range were found in biochar-500 ( $pK_a$  7.5), biochar-MX ( $pK_a$  7.3) and biochar-300 ( $pK_b$  7.0). Other anion-exchange groups have  $pK_b$  from 4.9 to 6.3 mEq/g, which characterizes them as weakly basic.

In alkaline environments, the ion exchange capacity of most biochar is more pronounced than in acidic environments. All biochar has an intense effect on the pH value; the maximum change is caused by biochar-MW.

Functioning at a pH of 7...8 as a weak acid, biochar can contribute to an acidic pH change, binding ammonia, which, according to some hypotheses, may be one of the factors contributing to the pH change in composting processes.

Based on these data, it can be assumed that Biochar-MW 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, biochar not only acts as acceptors of metal ions during the composting process, but also function as a soft regulator of the pH value.

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