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**CHEMICAL AND STRUCTURAL CHARACTERISTICS AND SORPTION PROPERTIES
BIOCHAR FROM WASTE COFFEE GROUNDS**Taisiia Sokolova³, Galyna Krusir^{1,2}, Ihor Petrushka³, Myroslav Malovanyy³, Valeriia Sokolova¹¹ Odesa National Technological University, St. Kanatna, 112, Odesa, Ukraine, 65039² Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences and Arts Northwestern Switzerland, Hofackerstrasse 30, 4132 Muttentz, Switzerland³ Lviv Polytechnic National University, Stepana Bendery 12, Lviv, Ukraine, 79000

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Abstract

The processing of waste coffee grounds is a global problem, and its transformation into a target secondary product is an urgent and promising task. The aim of the study is to produce biochar that can be used in the process of anaerobic digestion of food waste from a hotel and restaurant complex to produce biogas and to determine its sorption characteristics. The chemical composition of the raw materials and biochar obtained by pyrolysis and microwave irradiation showed that the proportion of lignin and ash increases with increasing temperature. Studies of the interaction of lead ions with plant material and its modified forms show that sorption by biochar is much higher than by raw materials, probably due to differences in chemical composition, surface properties, etc. Comparison of the data on the sorption of lead ions by modified forms (biochar) allows us to conclude that the method of preparation has a significant effect on the sorption value. The pyrolysis temperature of the biochar has a favourable effect on the sorption properties of the samples. The obtained adsorption isotherms are of the L-type. The maximum sorption values are observed under the experimental conditions at an initial concentration of lead ions of 1.00 mg/ml. The study of the kinetic parameters of the processes of lead ion sorption by biochar preparations based on the curve of residual lead ion concentrations shows that equilibrium in the system is achieved in a few hours. The maximum sorption values are observed after 2.5-3 hours of incubation.

Keywords: waste coffee sludge; biochar; sorption properties; environmental protection technologies.

**ХІМІЧНІ І СТРУКТУРНІ ХАРАКТЕРИСТИКИ ТА СОРЕБЦІЙНІ ВЛАСТИВОСТІ
БІОЧАРІВ З ВІДПРАЦЬОВАНОЇ КАВОВОЇ ГУЩІ**Таїсія Соколова³, Галина Крусір^{1,2}, Ігор Петрушка³, Мирослав Мальований³, Валерія Соколова¹¹ Одеський національний технологічний університет, вул. Канатна, 112, м. Одеса, Україна, 65039² Інститут екопідприємництва, Школа наук про життя, Університет прикладних наук та мистецтв Північно-Західної Швейцарії, Хофакерштрассе 30, 4132 Муттенц, Швейцарія³ Національний університет "Львівська політехніка", вул. Степана Бендері, 12, Львів, Україна, 79000**Анотація**

Переробка відпрацьованої кавової гущі – глобальна проблема, її перетворення в цільовий вторинний продукт є актуальною та перспективною задачею. Метою дослідження є отримання біовугілля, яке може бути застосовано в процесі анаеробного зброджування харчових відходів готельно-ресторанного комплексу для отримання біогазу, та визначення його сорбційних характеристик. За результатами хімічного складу сировини та біочарів, отриманих піролізом та мікрохвильовим опроміненням показали, що зі збільшенням температури збільшується доля лігніну та золи. Дослідження взаємодії іонів свинцю із рослинною сировиною та її модифікованими формами свідчать, що сорбція біочарами значно вища, ніж сировиною, ймовірно, завдяки відмінностям у хімічному складі, властивостях поверхні та ін. Зіставлення даних сорбції іонів свинцю модифікованими формами (біочарами) дозволяє зробити висновки про значний вплив методу отримання на величину сорбції. Температура піролізу біочару надає сприятливий вплив на сорбційні властивості зразків. Отримані ізотерми адсорбції відносяться до L-типу. Максимальні значення сорбції спостерігаються в умовах дослідів при початковій концентрації іонів свинцю 1.00 мг/мл. Дослідження кінетичних параметрів процесів сорбції іонів свинцю препаратами біочарів за перебігом кривої залишкових концентрацій іонів свинцю свідчить, що рівновага в системі досягається за кілька годин. Максимальні значення сорбції спостерігаються через 2.5–3 години інкубації.

Ключові слова: відпрацьована кавова гуща; біочар; хімічні властивості; структурні характеристики поверхні; сорбційні властивості; технології захисту навколишнього середовища.

*Corresponding author: e-mail: taiasokolova041@gmail.com

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Introduction

Every year, the amount of food waste (FW) from hotel and restaurant operations is increasing, the disposal and processing of which is not carried out properly, which causes pollution and anthropogenic pressure on the environment, adding a significant contribution to global warming [1]. Given the tendency for waste to accumulate in regions such as Europe, East, Central and South Asia, and the Pacific, experts note an increase in global waste to 2586 tonnes by 2030, and by 2050, these data are projected to reach 3401 tonnes [2]. Food waste includes spent coffee grounds (SCG), the accumulation of which is increasing rapidly due to the popularisation of coffee around the world, for example, according to the International Coffee Organization from 2021, coffee production for the period from 2019 to 2020 was 20 trillion kg, in 2022–2023, global production increased by 0.1% due to a decrease in production in Asia, Oceania and Africa, but for the period 2023–2024, consumption is projected to increase to 2.2 % of tonnes [3; 4]. Spent coffee grounds are one of the components of food waste in Ukraine, the utilisation and processing of which into a targeted secondary product is an urgent and promising task, given the volume of their accumulation. In addition to the coffee industry, spent coffee grounds are also a by-product of other industries, such as brewing [5]. Due to the fact that SCG is a valuable and organic-rich waste (cellulose, hemicellulose, lignin, etc.), research is developing to produce bioenergy from it as a potential source [6]. A number of studies have also been conducted to produce biochar from spent coffee sludge, which have had positive results [3].

Biochar is a solid, amorphous and carbon-rich residue after pyrolysis of biomass that is similar to charcoal with high porosity, higher specific surface area, higher aromaticity, a variety of functional groups, and contains hydrogen, oxygen, nitrogen, sulfur and ash [7; 8; 1].

Biochar is mainly characterised by three chemical elements in its composition, namely Carbon, Hydrogen and Nitrogen, which is approximately 44.03, 8.04 and 0.17 % respectively. The physicochemical characteristics (physical, chemical, spectral, morphological characteristics) of biochar are most influenced by temperature.

Biochar is produced using several technologies, such as slow pyrolysis (300–700 °C), fast pyrolysis (300–1000 °C), intermediate pyrolysis (300–500 °C), instantaneous carbonisation (300–600 °C), gasification (600–1500 °C), torrefaction

(200–300 °C), hydrothermal carbonisation (100–300 °C), microwave pyrolysis (350–650 °C (400–2700 W)). The difference between these technologies is not only in temperature, but also in the time of exposure of raw materials and the yield of biochar [9]. Slow and fast pyrolysis are considered to be the most common in experimental studies of these technologies, and slow pyrolysis is the most efficient in terms of biochar yield (21–80 %), and microwave pyrolysis (microwave irradiation) is also a promising area of research (15–80 %) [9]. During the pyrolysis process, functional groups are destroyed, which affects the biochar structure and chemical properties, while the atomic ratio of carbon increases with increasing pyrolysis temperature, and other atomic components such as hydrogen, oxygen, nitrogen and others decrease [10].

A large number of studies have been conducted on the above technologies, for example, it was proposed to use intermediate pyrolysis of chicken manure in a screw reactor at a temperature of 350 °C, heating rate of 4.5 °C/min, resulting in biochar with a yield of 55.7 % and a carbon content of 62 % [11]. The same technology was used to produce biochar with a yield of 19 % by pyrolysis of burdock grass at 600 °C and a heating rate of 50 °C/min [12].

For better biochar quality, namely the content of a higher percentage of carbon, high temperature plays an important role, due to the rapid removal of volatile compounds from the biomass of the feedstock, the technology of rapid pyrolysis of pine sawdust was used to obtain a yield of 70.68 to 78.75 % at a temperature of 550–750 °C [13].

The technology of slow pyrolysis of wheat straw yielded 94.8 wt%, and at a temperature of 750–900 °C and 30 minutes of woody biomass in the furnace, high-quality biochar was obtained, which can replace conventional coal [14].

The microwave assisted pyrolysis (MAP) is considered as an alternative to traditional biochar production technologies in reactors, it is more controllable than previous technologies, is a one-step process, and has cost and energy-efficient positive impacts. MAC generates heat through molecular motion, which is caused by the movement of ions and dipolar particles, this type of heating at the molecular level leads to rapid, efficient and homogeneous heating of the feedstock throughout the reactor [15]. The advantages and disadvantages of this technology have been analysed in studies of process parameters such as temperature [16; 17], mass

flow rate of raw materials [18], microwave power [19], heating rate [20; 21] and residence time of raw materials in the reactor [22; 16].

Food waste has also been actively used as a raw material for microwave pyrolysis, for example, at a temperature of 500 °C for 5 s, the process of burning food waste in garbage bags (LDPE) took place, the biomass yield was 61.25 wt. Based on this study, a quadratic polynomial model was developed to predict the biochar yield by varying various process parameters [23]. Biochar produced by microwave pyrolysis of kitchen waste with rice straw and ZnCl_2 as a sensor demonstrated a 1:1 ratio, low ash content combined with high calorific value (20.550 MJ/kg), high energy yield (55.944 %) and high fuel utilisation factor (< 5.267) [24]. Coffee sludge was also used in pyrolysis, which was carried out in the temperature range of 400–750 °C and a heating rate of 50 °C/s in a helium atmosphere, and the study resulted in the production of target products such as biogas and biochar [25]. Biochar was obtained from waste coffee sludge: biomass was dried at 90 °C overnight, then mixed with zinc chloride (ZnCl_2) in a ratio of 1:0.5 and pyrolysed at 900 °C for 1 hour at 10 °C/min. The resulting mass was washed with an aqueous solution of HCL (10 wt.%), and distilled water and ethanol (99.7 %), then dried at 60 °C overnight to obtain biochar [26].

Biochar from food waste is used as a clean fuel, for the extraction of pollutants and composting of organic waste, for the removal of heavy metals, for the production of building materials, and as an additive in methanogenesis [2; 27; 28].

Biochar is used in the anaerobic digestion of food waste to increase the efficiency and productivity of the biogas production process. This is due to microbial enrichment, increased buffering capacity and inhibition of ammonia by biochar, which can increase methane production by about 20 % and reduce the amount of accumulated VFAs if the process is carried out under mesophilic thermal conditions [29; 30; 31; 32; 33]

The aim of this study is to produce biochar, which can be used efficiently and effectively in the future during the process of anaerobic digestion of

food waste from a hotel and restaurant complex to produce biogas, and to determine its sorption characteristics.

To achieve this goal, we need to solve the following tasks:

- 1) to provide a comparative chemical composition of raw materials and biochar obtained using thermal and microwave methods;
- 2) determine the granulometric composition of biochar after grinding;
- 3) assessment of the sorption activity of plant material and biochar obtained from it;
- 4) studying the adsorption isotherms of lead acetate by raw materials and biochar preparations;
- 5) determination of the sorption constants of lead ions by biochar;
- 6) studying the effect of lead ion concentration on the amount of their sorption by biochar;
- 7) studying the kinetic parameters of lead ion sorption by biochar;
- 8) determine the structural characteristics of the surface of biochar and raw materials.

Material and methods

Raw materials

The biochar was produced from spent coffee sludge from the Zucchini restaurant (Odesa, Ukraine), which was collected over three working days during the summer season of its operation.

Two types of biochar production were used: thermal pyrolysis and microwave pyrolysis (microwave irradiation). The feedstock, waste coffee sludge, was washed with deionised water and then dried at 105 °C for 24 hours and stored in a sealed container.

Methods

Preparation of biofuels by pyrolysis: 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. Then, the feedstock samples were kept at 300 °C and 500 °C for 30 minutes. The resulting biofuels were labelled with heating temperatures as biochar-300 and biochar-500, respectively.

The carbonation process was carried out in the experimental laboratory setup shown in Figure 1.

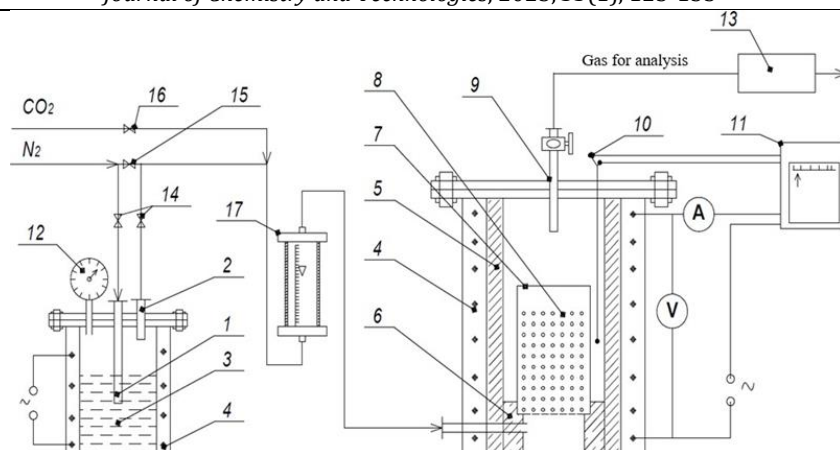


Fig. 1. Schematic of the experimental setup for carbonisation of coffee sludge and activation of carbonate
 1 – nitrogen inlet pipe; 2 – nitrogen-water vapour mixture outlet pipe; 3 – steam generator; 4 – electric heater; 5 – reactor; 6 – stop ring; 7 – reaction flask with perforated bottom; 8 – raw material; 9 – gas outlet pipe; 10 – thermocouple; 11 – KS-2 device; 12 – manometer; 13 – gas analyzer; 14, 15, 16 – valves; 17 – flow meter

After washing and drying, a sample of coffee sludge (40 g) 8 is placed in a perforated bottom reaction beaker 7. With the valves 14 and 16 closed, open 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 monitored using a thermocouple 10. The resulting pyrolysis gas is

analysed for component content using a Gasboard 3100R 13 gas analyser.

The resulting carbonised product is grey in colour and retains its original morphological shape.

For microwave pyrolysis (microwave irradiation), a conventional Beko microwave oven with a microwave power of 800 W was used, in which pyrolysis took place for 15 minutes (Fig. 2).



Fig. 2. Beko microwave oven with a microwave power of 800 W

A microwave digestion system with a maximum power of 800 W and a temperature of 230 °C, as shown in Figure 2, was used for the biochar experiments. Firstly, deionised water and spent coffee grounds were placed in the reactor vessel at the desired biomass to water ratio (1 : 2), and then the vessel was tightly closed. Then, the parameters of the experiment process were set (temperature – 230 °C, holding time – 15 minutes), after which 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 in an oven at 105 °C for 24 hours. The resulting biofuel was

labelled by the method of production as biochar-MX.

After carbonisation, the material was subjected to grinding in a ball mill, followed by particle size classification.

All experiments and performance analyses were carried out in triplicate.

Biopolymer composition of the samples: hemicelluloses (HMC) were determined by treating biochar samples with hydrochloric acid with a mass fraction of 2 % according to the method of hydrolysis of easily hydrolysed polysaccharides [34; 35]. The amount of reduction of hydrolysates (Hagedron-Jensen method) multiplied by a factor of 0.88 was used to estimate the content of HMCs [36]. Cellulose was determined by hydrolysing the residue after

removal of HMCs with sulfuric acid according to the method of hydrolysis of polysaccharides that are difficult to hydrolyse in the presence of 85 % sulfuric acid for 5 hours at a temperature of 1000 °C. Reducing substances were determined in the hydrolysates and multiplied by a factor of 0.9 [37].

Total nitrogen was determined by the Kjeldahl method [38], and protein was determined by multiplying total nitrogen by the appropriate factor. Lignin was determined as the residue after hydrolysis of cellulose. Lipids were determined by gravimetric extraction with a non- polar solvent. Ash was determined by the gravimetric method.

°C. Measurements of the differences in mercury

=

where: ΔL is the elongation of the quartz helix depending on the mass of the sorbent; Δl is the

$$P/P_s a(I - P/P_s) = I a_m C + C - I a_m C P/P_s,$$

P_s – saturated vapour pressure at a given
 P/P_s – relative vapour pressure; a – surface
 a_m – surface concentration of sorbate when all

– saturated vapour pressure at a given
 P/P_s – relative vapour pressure; a – surface
concentration of sorbate; a_m – surface

$$S_{yg} = a_m \cdot N_A \cdot S_0 \cdot 10^{-23},$$

$$S = \frac{v_{max}}{2 S_{yg}}$$

v_{max} – maximum amount of moisture that can be

Sorption of lead ions – the test samples (0.25 g) were placed in a solution of lead acetate with a concentration of 0.01 mol/l, hydromodule 20. In the blank experiment, the samples were placed in distilled water. The preparations were kept in solutions of lead salt for 17 hours (time of establishment of sorption equilibrium) at 37 °C, and then the concentration of lead ions in the filtrates was determined spectrophotometrically [40]. The amount of lead sorption was determined

by the difference between the initial and residual concentrations of lead ions in solution.

Adsorption isotherms - to determine the adsorption isotherms, the same biochar weights (0.1 g) were placed in a solution of lead acetate (0.25–2.0 mg/ml). After 2.5 hours of incubation with constant stirring at 20 °C, the residual concentration of lead acetate was determined and for each concentration the amount of sorbate absorbed per unit mass (0.1 g) of sorbent, i.e. the specific capacity of the sorbent, was calculated. The amount of lead acetate adsorbed by 1 g of biochar was calculated by the formula:

$$G = ((C_0 - C_{\text{equilibrium}}) \cdot a) / B,$$

where C_0 is the initial concentration of lead acetate, mg/ml; $C_{\text{equilibrium}}$ is the residual (equilibrium) concentration of lead acetate, mg/ml; a is the volume of lead acetate solution added to the biochar sample, ml; B is the weight of the biochar, g.

The results obtained are presented graphically – the specific capacity of the sorbent (mg/g) was plotted on the ordinate axis, and the corresponding values of the residual concentration ($C_{\text{equilibrium}}$, mg/ml) were plotted on the abscissa axis.

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

Results and Discussion

Most waste from the food industry and agriculture is lignocellulosic materials, consisting of cellulose, hemicelluloses 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 are joined together to form branched molecules with long chains. It serves as a binder for gluing cellulose fibres together [41].

The organic compounds present in biomass decompose at a certain temperature in an environment with limited oxygen supply. Factors that affect the pyrolysis product include process temperature, residence time, biomass type, and heating rate [42; 43]. Initially, hemicelluloses decompose at 220 °C, with decomposition mostly complete at 315 °C. Cellulose begins to decompose at temperatures above 315 °C and by 400 °C all cellulose is converted to non-condensable gas and condensable organic vapours. Lignin starts to decompose at 160 °C, but the process is slow and

decomposition continues until it reaches 900 °C [44].

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.

Table 1

Results of determining the chemical composition of raw materials and biochar samples						
Biomass	Protein, (%)	Lipids, (%)	Hemicellulose, (%)	Pulp, (%)	Lignin, (%)	Ash, (%)
Coffee grounds (raw material)	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

According to the results of determining the chemical composition of raw materials and biochars 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 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

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

Table 1 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.

Prediction of the effect of biochar in various processes where it is used is based on the control of a number of quality indicators, the main place among which is occupied by sorption properties.

Biochar is known to be an effective sorbent for environmental pollutants, such as heavy metal ions, oil and oil products, microbiological pollutants, etc.

The table presents the results of determining the sorption of Pb ions²⁺ raw materials and biochar obtained by various physical methods (Table 3).

Table 3

Sorption of lead ions by biochar and raw materials		
Sample	Sorption of Pb ²⁺	
	mg/g nose.	% of output.
Coffee grounds	8/6±0.02	21.5±0.28
Biochar-300	12.8±0.07	34.5±0.41
Biochar-500	13.3±0.12	35.7±0.06
Biochar-MX	10.9±0.05	29.2±0.17

Studying the interaction of lead ions with plant material and its modified forms, we characterised the patterns of their sorption by these enterosorbents. The results obtained (Table 3) indicate that the sorption by modified forms is much higher than by plant material, probably due to differences in chemical composition, surface properties, etc.

Comparison of the data on the sorption of lead ions by modified forms (biochar) allows us to draw conclusions about the significant influence of the method of preparation on the sorption value.

The pyrolysis temperature of the biochar has a favourable effect on the sorption properties of the samples, with an increase in temperature increasing the sorption properties.

The most appropriate approach to studying the adsorption mechanism is to study adsorption isotherms. Important characteristics of adsorption are: a) adsorption rate; b) shape of the isotherm; c) presence of plateaus on many isotherms; d) degree of solvent adsorption; e) type of adsorption – multilayer or monolayer; f) orientation of adsorbed molecules; g) effect of temperature; h) nature of interaction between adsorbate and adsorbent.

The adsorption isotherms shown in Fig. 3, can be attributed to the L-type. The adsorption processes corresponding to this type of isotherms are characterised by negligible interaction between the adsorbed molecules, when the activation energy does not depend on the degree of surface coverage. This type of isotherms is caused by the parallel orientation of the solute molecules [45]. In the initial section, the class L isotherms are concave with respect to the concentration axis.

Langmuir's equation was used to interpret the isotherms of lead ion sorption by biochar:

$$a = \frac{a_m \cdot K \cdot C}{1 + K \cdot C}$$

where C is the equilibrium concentration of lead acetate in solution, mol/l;

a is the amount of lead acetate in moles sorbed by a unit mass of biochar, mol/g;

a_m is the sorption capacity constant, which characterises the maximum amount of sorbate that can be monomolecularly sorbed by the sorbent;

K is the affinity constant, which characterises the strength of the forces involved in the interaction (affinity constant).

The experimental results were processed using the Langmuir equation in a linear form (Fig. 3). The results of estimating the value of sorption constants are presented in Table 4.

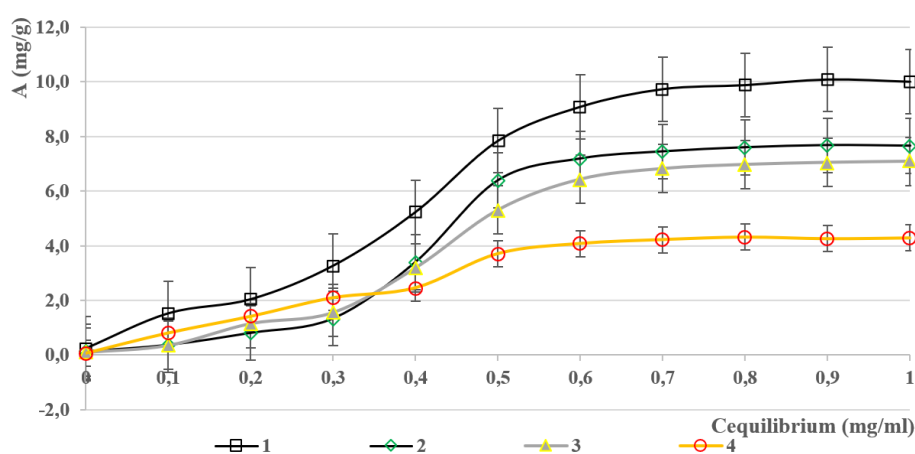


Fig. 3. Adsorption isotherms of lead acetate: 1) raw material; 2) biochar-300; 3) biochar-500; 4) biochar-MX

Table 4

Sorption constants of lead ions by biochar

Sorbent	Affinity constant, K , mol/l	Sorption capacity constant, a_m , mol/g
Biochar-300	358±1.44	0.042±0.002
Biochar-MX	374±1.63	0.078±0.004

Comparing the sorption capacity of biochar, based on the values of the sorption capacity constants a_m , it can be concluded that the surface of biochar-MX has a large number of sorption

centres capable of interacting with lead ions. Biochar-MX also forms strong bonds with lead ions.

Table 5

Effect of lead ion concentration on the amount of their sorption by biochar

Sample	Initial acid concentration, mg/ml		Sorption	
			mg/g of preparation	% of out.
Coffee grounds	0.25		0.7±0.03	10.7±0.07
	0.50		1.9±0.03	15.3±0.04
	0.70		3.5±0.04	20.1±0.03
	1.00		7.5±0.02	29.8±0.05
	2.00		13.8±0.08	27.6±0.07
Biochar-500	0.25		0.7±0.03	10.8±0.11
	0.50		2.2±0.01	17.4±0.02
	0.70		5.1±0.04	29.3±0.13
	1.00		10.1±0.02	40.5±0.23
	2.00		19.9±0.11	39.8±0.24
Biochar-300	0.25		0.5±0.07	8.2±0.06
	0.50		1.4±0.12	10.9±0.14
	0.70		4.3±0.19	24.8±0.13
	1.00		7.5±0.09	30.1±0.08

Continuation of Table 5

Biochar-MX	2.00	14.6±0.16	29.1±0.09
	0.25	0.6±0.08	9.1±0.08
	0.50	2.3±0.02	18.3±0.19
	0.70	5.3±0.06	30.4±0.07
	1.00	10.1±0.04	40.3±0.07
	2.00	16.4±0.10	32.8±0.09

The results of experimental studies on the effect of the concentration of lead ions on the value of their sorption by biochar, presented in Table 5, show that the maximum sorption values are observed under the experimental conditions at an initial concentration of lead ions of 1.00 mg/ml. The analysis of the sorption isotherms of lead ions by biochar samples, the graphical solution of the

Langmuir equation, which gives a direct proportional dependence in the coordinates: equilibrium acid concentration – the ratio of the equilibrium concentration to the sorption value (Fig. 4), and the calculation of sorption constants confirm the adequacy of the studied process to the Langmuir theory of monomolecular adsorption.

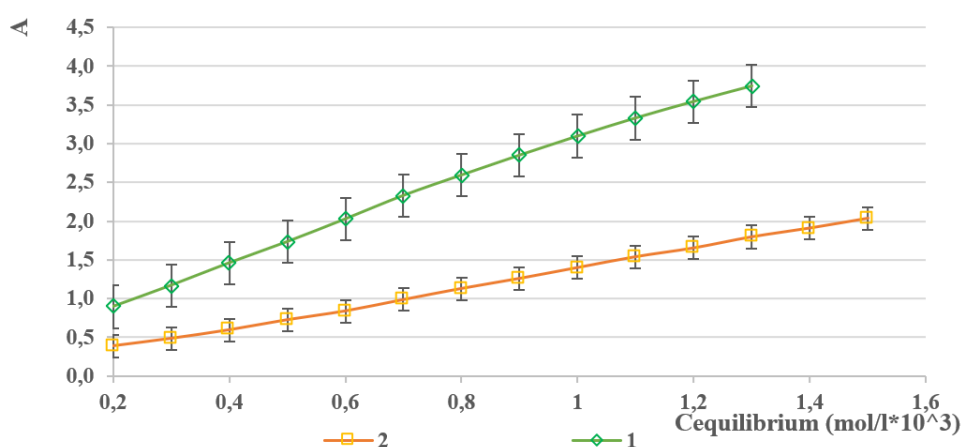


Fig. 4. Dependence of equilibrium concentration of lead acetate on the ratio of equilibrium concentration to sorption value: 1 – Biochar-500; 2 – coffee sludge

Kinetics of lead ion sorption by biochar

Fig. 5 shows the characteristic course of the curve of residual lead ion concentrations, and it can be seen that equilibrium in the system is reached in a few hours. Based on one of the consequences of the general theory of diffusion-controlled processes, the relationship between the residual concentration c_t and the square root of time $\sqrt{t}$ there is a linear relationship between the residual concentration and the root of the time. The linearisation of the residual concentration

curve makes it possible to compare sorption rate constants, defined as the ratio of the amount of sorbed material (P) to the mass of sorbent (m), and the square root of time:

$$K = \frac{P}{m\sqrt{t}}$$

Graphically, K is determined by the slope of the residual curve

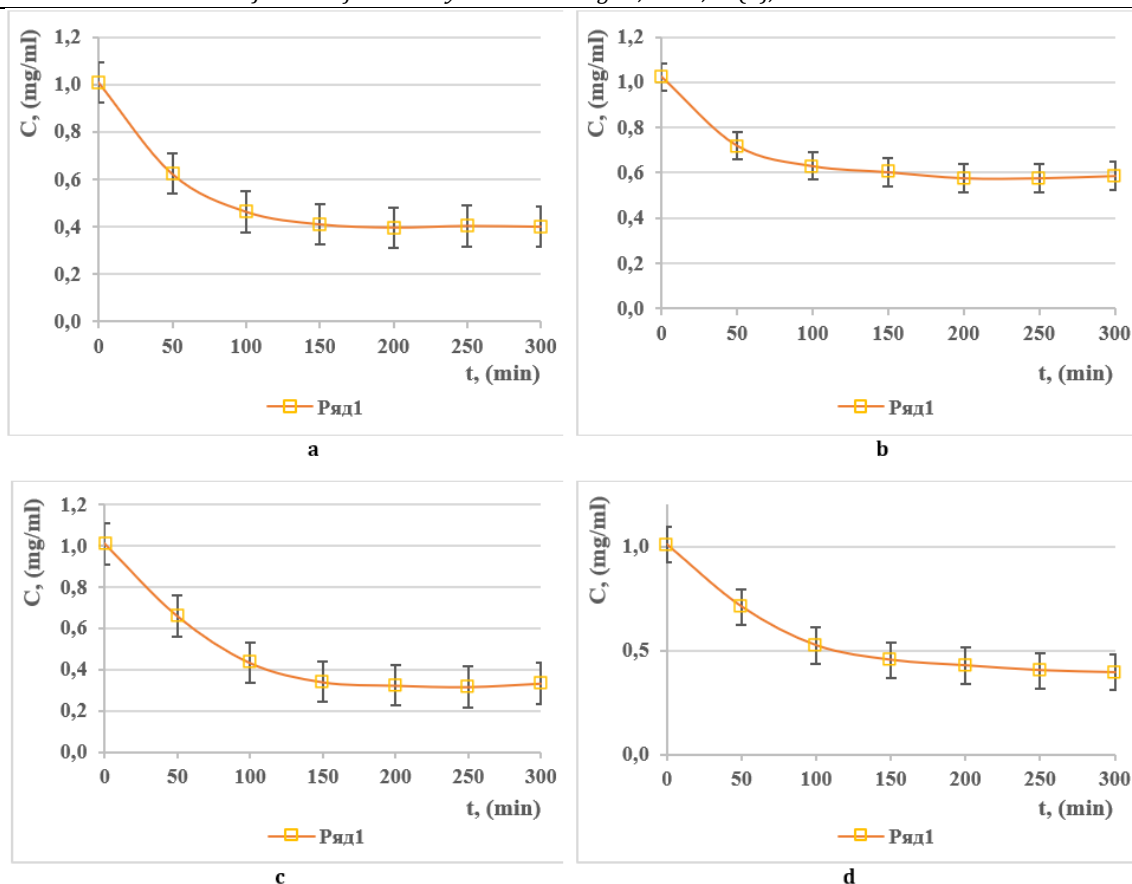


Fig. 5. Dependence of residual lead ion concentrations on incubation time on raw materials and biochar samples: a – on raw materials; b – on biochar-300; c – on biochar-500; d – on biochar-MX in 0.1% lead ion solution

The amount of material (Q) sorbed by a unit mass of sorbent ($Q = \frac{P}{t}$) is linearly related to $\sqrt{t}$:

$$Q = K \cdot \sqrt{t}.$$

If we differentiate this expression by dt , we obtain the sorption rate (v):

$$v = \frac{dQ}{dt} = \frac{K}{2\sqrt{t}}$$

Table 6

Sorption rate of lead ions by raw materials and biochar	
Sample	Sorption rate, mg/g min
Coffee grounds	0.065±0.0038
Biochar-300	0.085±0.0048
Biochar-500	0.098±0.0024
Biochar-MX	0.1025±0.0004

The results of determining the rate of sorption of lead ions by raw materials and biochar (Table 6) indicate that the rate of sorption of lead ions increases with increasing pyrolysis

temperature. The highest rate of lead ion sorption is observed for biochar obtained by microwave irradiation.

Table 7

Influence of incubation time on the amount of lead ion sorption by plant preparations			
Sample	Sorption time, min	Sorption	
		mg/g of preparation	% of output.
Coffee grounds	30	2.8±0.03	11.4±0.03
	60	4.5±0.04	18.3±0.05
	120	6.3±0.01	25.6±0.02
	180	7.4±0.03	29.9±0.08
	240	7.5±0.02	30.2±0.14
	360	7.5±0.03	30.4±0.04
Biochar-300	30	1.0±0.02	3.8±0.03
	60	5.2±0.05	20.8±0.04
	120	9.3±0.08	37.4±0.02
	180	10.1±0.05	40.7±0.03

			<i>Continuation of Table 7</i>
Biochar-500	240	10.4±0.17	41.8±0.04
	360	10.7±0.08	43.1±0.40
	30	1.8±0.09	7.4±0.17
	60	4.9±0.05	20.1±0.03
	120	7.4±0.06	29.7±0.05
	180	8.4±0.01	33.8±0.02
Biochar HB	240	8.6±0.08	34.8±0.20
	360	8.7±0.06	35.1±0.03
	30	2.6±0.03	10.4±0.03
	60	6.4±0.01	25.7±0.04
	120	9.8±0.29	39.5±0.06
	180	10.1±0.10	40.6±0.05
	240	10.4±0.12	41.9±0.21
	260	10.5±0.10	42.2±0.02

Based on the data presented in Table 7 on the effect of the duration of incubation of biochar in solutions of lead ions on the value of their sorption by biochar, it can be concluded that the maximum sorption values are observed after 2.5–3 hours of incubation. The value of lead ion sorption by Biochar-300 is 40.7 % after 3 hours of their joint incubation. An increase in the interaction time does not lead to a significant increase in the degree of lead ion sorption by plant material and its modified forms.

Conclusions

Prediction of the effect of biochar in various processes where it is used is based on the control of a number of quality indicators, the main place among which is occupied by sorption properties.

According to the results of determining the chemical composition of raw materials and biochars 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.

After grinding, the highest content (83.5 % by weight) in carbonitic acid is characterised by a fraction of particles with a size of < 0.1 mm.

Studies of the interaction of lead ions with plant material and its modified forms show that sorption by modified forms is much higher than by plant material, probably due to differences in chemical composition, surface properties, etc.

Comparison of the data on the sorption of lead ions by modified forms (biochar) allows us to draw conclusions about the significant influence of the method of preparation on the sorption value.

The pyrolysis temperature of the biochar has a favourable effect on the sorption properties of the samples, with an increase in temperature increasing the sorption properties.

The most appropriate approach to studying the adsorption mechanism is to study adsorption isotherms.

The obtained adsorption isotherms are of the L-type. The adsorption processes corresponding to this type of isotherms are characterised by negligible interaction between the adsorbed molecules, when the activation energy does not depend on the degree of surface coverage. This type of isotherms is caused by the parallel orientation of the solute molecules. In the initial section, the class L isotherms are concave with respect to the concentration axis.

Comparing the sorption capacity of biochar, based on the values of the sorption capacity constants a_m , it can be concluded that the surface of biochar-MX has a large number of sorption centres capable of interacting with lead ions. Biochar-MX also forms strong bonds with lead ions.

The results of experimental studies on the effect of lead ion concentration on the amount of their sorption by biochar show that the maximum sorption values are observed under the experimental conditions at an initial concentration of lead ions of 1.00 mg/ml.

The analysis of the sorption isotherms of lead ions by biochar samples, the graphical solution of the Langmuir equation, which gives a direct proportional dependence in the coordinates: equilibrium acid concentration - the ratio of equilibrium concentration to the sorption value, and the calculation of sorption constants confirm the adequacy of the studied process to the Langmuir theory of monomolecular adsorption.

The study of the kinetic parameters of the processes of lead ion sorption by biochar preparations based on the curve of residual lead ion concentrations shows that equilibrium in the system is achieved in a few hours. The results of determining the rate of sorption of lead ions by raw materials and biochar indicate that the rate of

sorption of lead ions increases with increasing pyrolysis temperature. The highest rate of lead ion sorption is observed for biochar obtained by using microwave irradiation.

Based on the data on the effect of the duration of incubation of biochar in solutions of lead ions on the value of their sorption by biochar, it can be concluded that the maximum sorption values are observed after 2.5–3 hours of incubation. The value of lead ion sorption by Biochar-300 is

40.7 % after 3 hours of their joint incubation. An increase in the interaction time does not lead to a significant increase in the degree of lead ion sorption by plant material and its modified forms. In addition to the possibility of using the obtained biochar from waste coffee grounds as an additive in the anaerobic digestion process, given the obtained sorption results (up to 30 %), it is advisable to use biochar as an independent sorbent.

References

- [1] Premchand, P., Demichelis, F., Chiaramonti, D., Bensaid, S., Fino, D. (2023). Study on the effects of carbon dioxide atmosphere on the production of biochar derived from slow pyrolysis of organic agro-urban waste. *Waste Management*, 172, 308–319. <https://doi.org/10.1016/j.wasman.2023.10.035>
- [2] Awogbemi, O., Vandi Von Kallon, D. (2023). Progress in agricultural waste derived biochar as adsorbents for wastewater treatment. *Applied Surface Science Advances*, 18, 100518. <https://doi.org/10.1016/j.apsadv.2023.100518>
- [3] Pambudi, S., Saechua, W., Jongyingcharoen, J.S. (2024). A thermogravimetric assessment of eco-friendly biochar from oxidative torrefaction of spent coffee grounds: Combustion behavior, kinetic parameters, and potential emissions. *Environmental Technology & Innovation*, 33, 103472. <https://doi.org/10.1016/j.eti.2023.103472>
- [4] International Coffee Organization. (2023). *Coffee report and outlook*. <https://icocoffee.org/documents/cy2023-24/>
- [5] Atabani, A. E., Al-Muhtaseb, Aa. H., Kumar, G., Saratale G. D., Aslam, M., Khan, H. A., Said, Z., Mahmoud, E. (2019). Valorization of spent coffee grounds into biofuels and value-added products: pathway towards integrated bio-refinery. *Fuel*, 254, 115640. <https://doi.org/10.1016/j.fuel.2019.115640>
- [6] Sokolova, T., Krusir, G., Hugl, C., Breitenmoser, L., Yeleuova, E., Daldabayeva, G., Malovanny, M., Korkach, O., Sokolova, V. (2024). Study of the effect of biochar from spent coffee grounds on anaerobic digestion of food waste from the restaurant industry. *Journal of Chemistry and Technologies*, 32, 2. <https://doi.org/10.15421/jchemtech.v32i2.297925>
- [7] Jha, S., Nanda, S., Acharya, B., Dalai, A. K. (2022). A review of thermochemical conversion of waste biomass to biofuels. *Energies*, 15, 6352. <https://www.scopus.com/record/display>
- [8] Rawat, S., Boobalan, T., Sathish, M., Hotha, S., Thallada, B. (2023). Utilization of CO₂ activated litchi seed biochar for the fabrication of supercapacitor electrodes. *Biomass Bioenergy*, 171, 106747. <https://doi.org/10.1016/j.biombioe.2023.106747>
- [9] Safarian, S. (2023). Performance analysis of sustainable technologies for biochar production: A comprehensive review. *Energy Reports*, 9. <https://doi.org/10.1016/j.egyr.2023.03.111>
- [10] Fenta, A. A. (2024). State of the art of biochar in Ethiopia. A review. *Heliyon*, 10, 3, e24934. <https://doi.org/10.1016/j.heliyon.2024.e24934>
- [11] Morgano, M. T., Bergfeldt, B., Leibold, H., Richter, F., Stapf, D. (2018). Intermediate pyrolysis of agricultural waste: A decentral approach towards circular economy. *Chem. Eng.*, 65. <https://www.researchgate.net/publication/326031776>
- [12] Mohammed, I. Y., Abakr, Y. A., Yusup, S., Kazi, F. K. (2017). Valorization of Napier grass via intermediate pyrolysis: Optimization using response surface methodology and pyrolysis products characterization. *J. Clean. Prod.*, 142. <https://doi.org/10.1016/j.jclepro.2016.11.099>
- [13] Zhao, B., O'Connor, D., Zhang, J., Peng, T., Shen, Z., Tsang, D. C., Hou, D. (2018). Effect of pyrolysis temperature, heating rate, and residence time on rapeseed stem derived biochar. *J. Clean. Prod.*, 174. <https://doi.org/10.1016/j.jclepro.2017.11.013>
- [14] Mousa, E., Wang, C., Riesbeck, J., Larsson, M. (2016). Biomass applications in iron and steel industry: An overview of challenges and opportunities. *Renew. Sustain. Energy Rev.*, 65. <https://doi.org/10.1016/j.rser.2016.07.061>
- [15] Huang, Y.-F., Chiueh, P.-T., Lo, S.-L. (2016). A review on microwave pyrolysis of lignocellulosic biomass. *Sustain. Environ. Res.*, 26. <http://dx.doi.org/10.1016/j.serj.2016.04.012>
- [16] Liew, R. K., Nam, W. L., Chong, M. Y., Phang, X. Y., Su, M. H., Yek, P. N. Y., Ma, N. L., Cheng, C. K., Chong, C. T., Lam, S. S. (2018). Oil palm waste: An abundant and promising feedstock for microwave pyrolysis conversion into good quality biochar with potential multi-applications. *Process Safety and Environmental Protection*, 115. <https://doi.org/10.1016/j.psep.2017.10.005>
- [17] Wallace, C. A., Afzal, M. T., Saha, G. C. (2019). Effect of feedstock and microwave pyrolysis temperature on physio-chemical and nano-scale mechanical properties of biochar. *Bioresour. Bioprocess.*, 6. <https://scholar.google.com/scholar>
- [18] Huang, Y. - F., Chiueh, P.-T., Shih, C. - H., Lo, S.-L., Sun, L., Zhong, Y., Qiu, C. (2015). Microwave pyrolysis of rice straw to produce biochar as an adsorbent for CO₂ capture. *Energy*, 84. <https://doi.org/10.1016/j.energy.2015.02.026>
- [19] Kostas, E. T., Durán-Jiménez, G., Shepherd, B. J., Meredith, W., Stevens, L. A., Williams, O. S. A., Lye, G. J., Robinson, J. P. (2020). Microwave pyrolysis of olive pomace for bio-oil and bio-char production. *Chem. Eng. J.*, 387, 123404. <https://doi.org/10.1016/j.cej.2019.123404>
- [20] Hossain, M. A., Jewaratnam, J., Ganesan, P., Sahu, J., Ramesh, S., Poh, S. (2016). Microwave pyrolysis of oil palm fiber (OPF) for hydrogen production: parametric investigation. *Energy Convers. Manage.*, 115. <https://doi.org/10.1016/j.enconman.2016.02.058>
- [21] Sahoo, D., Remya, N. (2020). Influence of operating parameters on the microwave pyrolysis of rice husk: biochar yield, energy yield, and property of biochar.

- Biomass Convers. Biorefinery*, 1-10. <https://scholar.google.com/scholar>
- [22] Fodah, A. E. M., Ghosal, M. K., Behera, D. (2021). Solar-powered microwave pyrolysis of corn stover for value-added products and process techno-economic assessment. *Int. J. Energy Res.*, 45. <https://doi.org/10.1002/er.6192>
- [23] Neha, S., Remya, N. (2023). Optimization of biochar production from microwave co-pyrolysis of food waste and low-density polyethylene. *Original Article*, 13. <https://link.springer.com/article/10.1007/s13399-023-03948-w>
- [24] Nyambura, S. M., Li, C., Li, H., Xu, J., Wang, J., Zhu, X., Feng, X., Li, X., Bertrand, G. V., Ndumia, J. N., Chin, B. L. F. (2023). Microwave co-pyrolysis of kitchen food waste and rice straw: Effects of susceptor on thermal, surface, and fuel properties of biochar. *Fuel*, 352, 129093. <https://doi.org/10.1016/j.fuel.2023.129093>
- [25] Matrapazi, V. K., Zabanitout, A. (2020). Experimental and feasibility study of spent coffee grounds upscaling via pyrolysis towards proposing an eco-social innovation circular economy solution. *Science of The Total Environment*, 718, 137316. <https://doi.org/10.1016/j.scitotenv.2020.137316>
- [26] Hassan, A., Ding, W., Aslam, M. A., Bian, Y., Liu, Q., Sheng, Z. (2020). Microwave absorption property of coffee waste bio-carbon modified by industrial waste MnFe₂O₄ particles. *Journal of Materials Research and Technology*, 9, 6. <https://doi.org/10.1016/j.jmrt.2020.09.015>
- [27] Sharma, P., Bano, A., Verma, K., Yadav, M., Varjani, S., Singh, S. P., Tong, Y. W. (2023). Food waste digestate as biofertilizer and their direct applications in agriculture. *Bioresource Technology Reports*, 23, 101515. <https://doi.org/10.1016/j.biteb.2023.101515>
- [28] Saravanan, A., Karishma, S., Kumar, P. S., Rangasamy, G. (2023). A review on regeneration of biowaste into bio-products and bioenergy: Life cycle assessment and circular economy. *Fuel*, 338, 127221. <https://doi.org/10.1016/j.fuel.2022.127221>
- [29] Chiappero, M., Norouzi, O., Hu, M., Demichelis, F., Berruti, F., Di Maria, F., Mašek, O., Fiore, S. (2020). Review of biochar role as additive in anaerobic digestion processes. Re-new. *Sustain. Energy Rev.* <https://doi.org/10.1016/j.rser.2020.110037>
- [30] Qiu, L., Deng, Y. F., Wang, F., Davaritouchaee, M., Yao, Y. Q. (2019). A review on biochar-mediated anaerobic digestion with enhanced methane recovery. *Renew. Sustain. Energy Rev.* <https://doi.org/10.1016/j.rser.2019.109373>
- [31] Kumar, M., Dutta, S., You, S., Luo, G., Zhang, S., Show, P. L., Sawarkar, A. D., Singh, L., Tsang, D. C. W. (2021). A critical review on biochar for enhancing biogas production from anaerobic digestion of food waste and sludge. *J. Clean. Prod.* 305, 127143. <https://doi.org/10.1016/j.jclepro.2021.127143/>
- [32] Liang, J., Luo, L., Li, D., Varjani, S., Xu, Y., Wong, J. W. C. (2021). Promoting anaerobic codigestion of sewage sludge and food waste with different types of conductive materials: performance, stability, and underlying mechanism. *Bioresour. Technol.* 337, 125384. <https://doi.org/10.1016/j.biortech.2021.125384>
- [33] Li, Q., Xu, M., Wang, G., Chen, R., Qiao, W., Wang, X. (2017). Biochar assisted thermo-philic co-digestion of food waste and waste activated sludge under high feedstock to seed sludge ratio in batch experiment. *Bioresour. Technol.* 249, 1009–1016. <https://doi.org/10.1016/j.biortech.2017.11.002>
- [34] Pan, W., Ouyang, H., Tan, X., Yan, S., Zhang, R., Deng, R., Gu, L., He, Q. (2023). Effects of biochar addition towards the treatment of blackwater in anaerobic dynamic membrane bioreactor (AnDMBR): Comparison among room temperature, mesophilic and thermophilic conditions. *Bioresource Technology*, 374, 128776. <https://doi.org/10.1016/j.biortech.2023.128776>
- [35] Krusir, G., Sagdeeva, O., Malovanyy, M., Shunko, H., Gnizdovskyi, O. (2020). Investigation of Enzymatic Degradation of Solid Winemaking Wastes. *J. Ecol. Eng.* 21(2):72-79. <https://doi.org/10.12911/22998993/116345>
- [36] Pillsbury, D. M., Kulchar, G. V., (1934). The use of the hagedorn-jensen method in the determination of skin glucose. *Journal of Biological Chemistry*. 106, 1. [https://doi.org/10.1016/S0021-9258\(18\)75485-9](https://doi.org/10.1016/S0021-9258(18)75485-9)
- [37] Zhang, M., Song, X., Deines, T. W., Pei, Z. J., Wang, D. (2014). A consistency mapping for the effects on enzymatic hydrolysis sugar yield using two sugar yield definitions in cellulosic biofuel manufacturing. *Renewable Energy*, 62. <https://doi.org/10.1016/j.renene.2013.07.014>
- [38] Aguirre, J. (2022). The Kjeldahl Method: 140 Years, Guildford, UK. <https://doi.org/10.1007/978-3-031-31458-2>
- [39] Zou, J., Fan, C., Jiang, Y., Liu, X., Zhou, W., Xu, H., Huang, L. (2021) A preliminary study on assessing the Brunauer-Emmett-Teller analysis for disordered carbonaceous materials. *Microporous and Mesoporous Materials*, 327, 111411. <https://doi.org/10.1016/j.micromeso.2021.111411>
- [40] Tarighat, M. A., Nabavi, M., Mohammadzadeh, M. R. (2015). Chemometrics-assisted spectrophotometric method for simultaneous determination of Pb²⁺ and Cu²⁺ ions in different foodstuffs, soil and water samples using 2-benzylspiro [isoindolone-1,5'-oxazolidine]-2',3,4'-trione using continuous wavelet transformation and partial least squares – Calculation of pKf of complexes with rank annihilation factor analysis. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 145. <https://doi.org/10.1016/j.saa.2015.02.048>
- [41] Chernov, N. K., Krusir, G.V., Kovalenko, O.V. (2010). Biocorrectors of digestive processes. *Monograph*. Odesa. 236 p.
- [42] Cha, J. S., Park, S. H., Jung, S. C., Ryu, C., Jeon, J. K., Shin, M. C., Park, Y. K. (2016). Production and utilization of biochar: a review, *J. Ind. Eng. Chem.* 40, 2016. 1–15. <https://doi.org/10.1016/j.jiec.2016.06.002>
- [43] Yaashikaaa, P. R., Kumar, P. S., Varjani, S. J., Saravanan, A. (2019). Advances in production and application of biochar from lignocellulosic feedstocks for remediation of environmental pollutants. *Bioresour. Technol.* 292, 122030. <https://doi.org/10.1016/j.biortech.2019.122030>
- [44] Sharma, A., Pareek, V., Zhang, D. (2015). Biomass pyrolysis—a review of modelling, process parameters and catalytic studies, *Renew. Sust. Energy. Rev.* 50, 1081–1096. <https://doi.org/10.1016/j.rser.2015.04.193>
- [45] Tenea, A., Dinu, C., Rus, P. A., Ionescu, I. A., Gheorghe, S., Iancu, V. I., Vasile, G. G., Pascu, L. F., Chiriac, F. L. (2024). Exploring adsorption dynamics of heavy metals onto varied commercial microplastic substrates: Isothermal models and kinetics analysis. *Heliyon*. 10, 15. <https://doi.org/10.1016/j.heliyon.2024.e35364>

