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ORIGINAL ARTICLE

Wheat dust and extracted rapeseed scrap biochar: a comprehensive characterization and assessment of potential utilization in the context of the circular economy

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Abstract

The current utilization of wheat dust (WD) and hexane-extracted rapeseed scrap (RS) in Central Europe is inefficient and non-ecological. Therefore, it is necessary to identify an appropriate waste treatment that supports the principles of the circular economy. For this reason, the aforementioned wastes were pyrolyzed, resulting in the production of biochars, which are commonly used as absorbents or soil amendments. These biochars were then steam activated, characterized, and evaluated for potential further suitable and sustainable utilization. The structure, porosity, specific surface area, and composition of bound functional groups, nutrients, toxic elements, cation exchange capacity (CEC), and pH were analyzed as important parameters for biochar applications. RS biochar contained high concentrations of nutrients (N 75.9, P 21.5, K 15.1, C 603, Ca 14.3, Mg 8.31, S 5.40 $g{\cdot}kg^{-1}$ wt. all). The CEC was remarkably high 87.0 $cmol{\cdot}kg^{-1}$ for the RS biochar. The SSA value increased in fivefold in both samples upon activation (11.0 $m^2{\cdot}g^{-1}$ for WD biochar and 0.8 $m^2{\cdot}g^{-1}$ for RS biochar). The pore depth increased in accordance with activation temperature. Alkanes, aromatics, and oxygenated groups were detected on the biochars surfaces, yet more evident in WD. WD biochar could be used as an adsorbent for organic pollutants because its structure, surface area, and representation of functional group predict high adsorption efficiency, especially after activation. Raw RS biochar is more suited to utilization as a soil amendment, due to its high concentration of nutrients. These utilizations of biochar support the circular economy, eliminate pollution, improve soil properties, and reduce the need for industrially produced fertilizers and sorbents.

Keywords Biochar · Waste biomass · Agricultural waste · Circular bioeconomy · Soil amendment · Adsorbent

1 Introduction

The biowastes utilization for biochar production by pyrolysis has received increasing attention due to its low cost and environmental friendliness [1]. Biochar is produced from several types of waste biomass. The composition of the produced biochar is contingent upon the selected raw biomass, mostly on their elemental composition and to disparate ratios of plant cell wall units (lignin, cellulose, and hemicellulose) [2]. The pyrolysis conditions, including temperature, holding time, and heating rate also significantly affects the quantity and properties of the formed products [3, 4].

Given its composition and properties, biochar has been employed in a multitude of applications [5]. This study focuses on the two most commonly used methods of biochar utilization, namely as an adsorbent and as a soil amendment. Depending on the raw biomass and pyrolysis conditions,

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the resulting biochar can have a desired porosity, high surface area with various bound functional groups allowing its utilization as an adsorbent [6–8]. The use of biochar as an alternative to activated carbon is gaining popularity [9], since it is considered a cleaner and cheaper material [10]. Furthermore, replacing industrially produced sorbents with this bio-sorbent brings several environmental benefits [11]. Efforts are exerted to increase the biochar adsorption capacity as much as possible [12]. This is accomplished by the surface activation, which results in structural alterations, an increase in porosity, and enhancement in the value of the specific surface area [9]. Biochar activation can be carried out by physical and/or chemical methods [13]. Moreover, pyrolysis and activation can be made into one-step (pyrolysis of biomass with chemical activators) or two-step processes (activation of biochar with activating agents) [14]. The physical activation of biochar is conducted using CO_2 [15], steam [16], microwave, or ultrasonic waves [17]. This method of activation primarily increases the surface porosity of the biochar [18]. Chemical activation is achieved by strong acids [18], bases [19], oxidants [20], or salts [21]. It is possible to modify the functional groups that are bonded to its surface and thereby produce a more specific sorption material, just by choosing an activating solution [20]. Biochar was successfully used for adsorption of toxic elements, dyes, pesticides, polycyclic aromatic hydrocarbons, and antibiotics [22].

Used as a soil amendment, biochar can improve soil properties in multiple ways [23]. Biochar has a large surface, which is particularly useful for microbial growth in soils [24]. The addition of biochar to soil also causes aeration, as heavy clay soil that can be lightened [25]. Due to its porosity, it increases the soil's ability to retain moisture and thus nutrients that are dissolved in [26]. Due to its elemental composition, it serves as a means of biological sequestration of carbon. Additionally, it facilitates the return of nutrients to the soil, thereby reducing their leaching [5]. The use of this type of fertilizer will also reduce the need for industrially produced fertilizers [27]. Reducing mineral fertilizer production and replacing them bring a lot of environmental benefits, such as organic farming, reduced carbon footprint, circular economy, and overall sustainable agriculture [23–26].

Based on previous research [28], two selected food wastes evaluated as the most suitable raw materials for sustainable and safe production biochar (the hexane extracted rapeseed scrap and wheat dust) were pyrolyzed. These waste biomasses, i.e., biochars produced from the upper mentioned raw materials, have not been studied yet. Some published works that dealt with waste from grain or rapeseed, however, focused only on the stems. Several published works deal with the characterization of biochars or the effect of pyrolysis conditions on their properties. However, they do not solve the question that arises—How to appropriately apply and utilize these materials? Therefore, a detailed analysis of the structure, surface, and composition of the tested biochars was performed as a key factor influencing its further application. It is well established that biochar is employed extensively as an adsorbent and soil amendment; therefore, these two applications were subjected to assessment. Moreover, in order to enhance the adsorption properties, both produced biochars were steam activated at two different temperatures. Finally, upon evaluating the results, recommendations on the proper subsequent utilization of the biochars were stated.

The work fills the gap about the utilization of biochar produced from unconventional local biowastes. The current work aims to (1) extensively characterize the biochars produced from wheat dust and rapeseed meal after extraction with hexane, (2) evaluate the effect of steam activation, and (3) evaluate their appropriate subsequent application based on their characterization. In contrast to studies that focus solely on the characterization of biochar or its utilization without evaluating the suitability of the application, this study takes a more comprehensive approach. It recommends the most suitable application based on the determined properties and composition of biochar. The study concludes with an outline of the probable costs associated with the production of these biochars.

2 Materials and methods

2.1 Raw biomass wastes

Wheat dust This waste is generated during the industrial production of wheat flour in mills. The waste material remains in the dust chamber, where grains are cleaned from dust and chaff. The wheat dust may contain small amounts of grain fragments and stems. Currently, the combustion of wheat dust results in undesirable emissions, ash, and the destruction of valuable components contained in the waste.

Extracted rapeseed scrap This waste material is produced during the industrial processing of rapeseed in oil factories. Subsequently, the harvested rapeseed was threshed, resulting in the separation of the straw and stem residue from the seeds. Subsequently, the seeds were pressed to extract the oil. The pressings that remained still contained residual oil that had not been pressed. The oil was subsequently recovered by hexane extraction, as the aforementioned waste material remained. Rapeseed scrap is the most commonly used as a feed additive or landfilled. However, feeding animals with hexane-soaked waste is not a convenient method.

A detailed analysis of the biomass waste used in this study was previously published [28].

2.2 Pyrolysis and surface activation

The pyrolysis device (Fig. S1, Supplementary Files) consisted of a tubular stainless-steel reactor (1 m length, 30 cm diameter) and was heated by a non-contact heater under nitrogen atmosphere. Biomass was transported through the unit by a screw conveyor at a speed of 2 $m \cdot h^{-1}$. Pyrolysis process was performed under operating conditions: heating rate 10 $°C \cdot min^{-1}$, final temperature 300 °C, and retention time 30 min.

The biochar surface was activated in an autoclave using steam at 350 °C and 450 °C with a holding time of 1 h without pressure increasing. The biochar and water mixture (1:4, m:m) was weighed into the autoclave.

Thus, the samples were further labelled as WD and RS for raw biochar (WD is biochar produced from wheat dust and RS from rapeseed scrap), WD350 and RS350 for activated biochar at 350 °C temperature, and WD450 and RS450 for activated biochar at 450 °C temperature.

2.3 Surface and structural analysis of biochar

Considering that biochar is mostly used as adsorption material, it was crucial to characterize its surface and structure. Scanning electron microscope (SEM) imaged the surface morphology. Pictures were taken by scanning electron microscope JSM-IT500HR (JEOL, Japan). Prior to analysis, samples were coated with a 5-nm layer of gold by plasma sputtering. Images were acquired with a secondary electron detector at a magnification of 500–3000 × in a vacuum, using an accelerating voltage of 15 keV and a working distance of 10 mm. The attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) was used to identify organic functional groups bounded on the surface of biochar. ATR spectra were taken by Nicolet 380 (Thermo Scientific, USA) in a wavenumber range of 400–4000 cm^{-1}. Prior to analysis, the samples were spread in agate mortar. Finally, N_2 adsorption/desorption isotherms and pore structure characteristics were measured at 77 K using an automatic adsorption instrument Quantachrome Autosorb-iQ-KR/MP-XR (Quantachrome Instruments Boynton Beach, USA). Prior to N_2 gas measurements, the samples were degassed at 110 °C in a vacuum for 24 h. Adsorption data were obtained over relative pressure. The specific surface area (SSA) of the sample was determined by employing the Brunauer, Emmett, and Teller (BET) method. The pore size distribution of the biochar was obtained through the application of the Brunauer, Emmett, and Teller (BJH) method.

2.4 Biochar elemental analysis

The dried samples were commuted in an agate mortar prior to analyzing. The subsequent elements were identified through the utilization of optical emission spectrometry with inductively coupled plasma (ICP-OES) methodology: Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Sr, Ti, V, and Zn. Elements were analyzed after acid digestion according to EN ISO 16968:2015 [29] in microwave digestion device M6 equipped with UHP10 rotor (PreeKem, China). The determination of selected elements was conducted using an ICP-OES 5110 VDV (Agilent, USA). For calibration purposes, multi-elemental standards AN9090MN, AN90401S (phosphorus), and AN90491H (sulfur) were employed (all Analytika s.r.o., Czech Republic). The determination of Hg was performed by AMA 254 (Altec, Czech Republic), working on the principle of the atomic absorption spectrometry. For calibration, Hg standard was used AN90241N (Analytika s.r.o., Czech Republic). Subsequently, elements C, N, and H were measured by Flash 2000 (Thermo Scientific, USA). The analysis of each sample was conducted in triplicate, and the resulting values were averaged. The standard deviation of these measurements was calculated, giving maximal relative standard deviation (RSD) 10% for all the analyzed samples.

2.5 Basic physico-chemical properties of biochar

In the raw biochar samples, cation exchange capacity (CEC) and pH value (H_2O) were determined according to EN ISO 23470:2019 [30] and EN ISO 10390:2021 [31], respectively. Each sample was analyzed two times, and the values were averaged ± standard deviation (SD) for CEC and ± 10% widespread uncertainty (U) for pH.

3 Results

3.1 Biochar surface and structure analysis

Biochars were prepared from different raw materials (Fig. S2, Supplementary Files).

3.1.1 ATR-FTIR spectra of biochar

ATR-FTIR analysis allows the identification of the functional groups bonded to the biochar surface. Figure 1 shows the ATR-FTIR spectrum for WD biochars and Fig. 2 for RS biochars.

Peaks that appeared within the 2900–2850 cm^{-1} range were attributed to the C–H stretching vibration of alkanes [32]. In both tested biochars, the intensity of these peaks decreased due to activation. A signal noise caused by CO_2 from the measurement background appeared in the area around 2300 cm^{-1} occurred in all obtained spectra. A wide area around 1700 cm^{-1} was obvious in all biochars samples.

Fig. 1 ATR-FTIR spectra of WD biochars, WD-raw wheat dust biochar, WD350-wheat dust biochar after steam activation at 350 °C, WD450-wheat dust biochar after steam activation at 350 °C

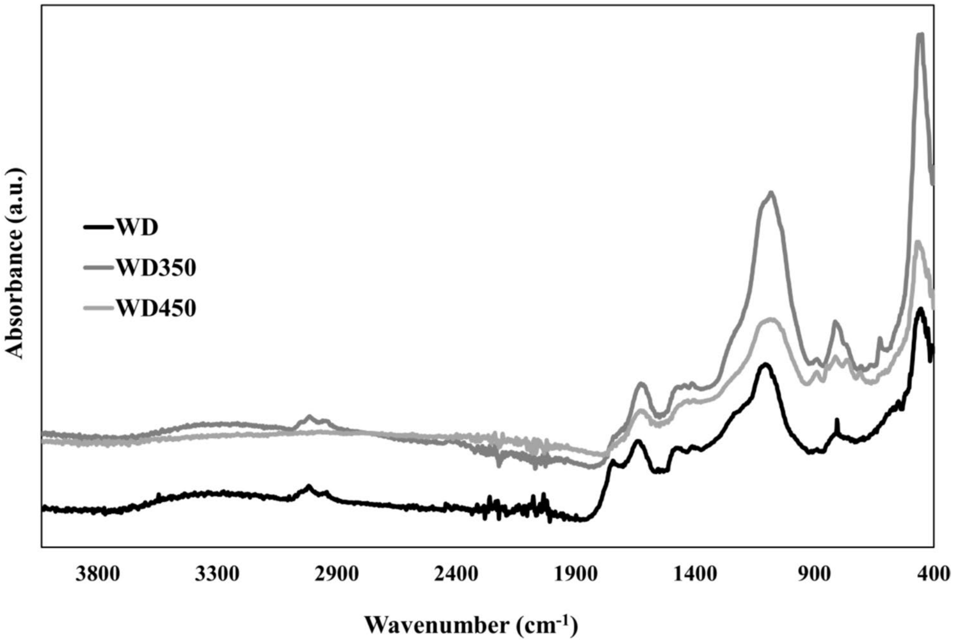
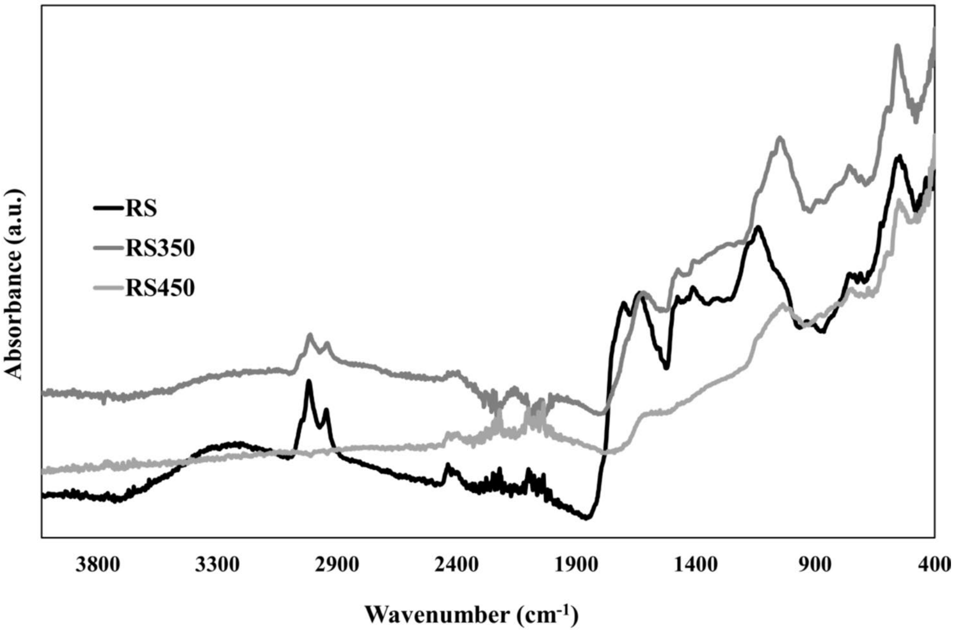


Fig. 2 ATR-FTIR spectra of RS biochars. RS, raw rapeseed scrap biochar; RS350, rapeseed scrap biochar after steam activation at 350 °C; RS450, rapeseed scrap biochar after steam activation at 350 °C



It was caused by C = O stretching vibration of various oxygen functional groups, probably from carboxylic acids or ketones [10]. In the case of WD biochar (Fig. 1), an increase in the intensity of these peaks due to surface activation was evident. For both types of tested biochar samples, peaks appeared around 1600 cm^{-1}. For the WD biochar sample, an increase in these peaks was again visible after surface activation. It can be attributed to stretching vibrations of C = C bonds in aromatic rings [33]. The bands located in the range from 1200 to 1000 cm^{-1} may indicate the presence of C-O stretching bonds in alcohols, phenols, acids, and ethers [34]. As a result of the activation, there was again an increased signal in WD biochar spectrum. Furthermore, the bands that appeared around 800 cm^{-1} can be assigned to C = C bending bonds into the aromatic ring [35] and out-of-plane bending vibrations of C–H bonds in the aromatic rings [36]. It has been reported that during the process of carbonization, the occurrence of the aromatization process may lead to the enhancement in the intensities of the above-mentioned peaks [37]. For WD biochar, the activation caused a substantial increase in intensity in these areas. Peaks occurring below 700 cm^{-1} can be assigned to the mineral matter (bonds with metals, semi-metals, non-metals, or halogens) present in the carbonaceous material structure [38].

3.1.2 Surface morphology and pore structure of biochar

As expected, the two types of biochar samples differ from each other (supplementary, Fig. S3-S8). WD biochar consisted of fine brown fragments with different shapes and sizes. The surface of the fragments was rough, and a fibrous structure was visible. Using a higher magnification, porous structure and tubes forming honeycomb can be seen. Following the application of steam, the formation of globular clusters of agglomerates was observed on the surface, while the porous structure remained intact. The crushing of biochar particles increases with higher activation temperature, due to the evolution of volatile matter. In contrast, RS biochar consisted of black solid agglomerates of diverse sizes that have a smooth surface. In higher resolution, it was noticeable that surface is wrinkled. The surface layer appears consistent, but holes can be seen in after zooming. However, it can be observed that in several places, the surface layer has been peeled off, and under which the spongy structure is hidden. At a higher activation temperature, the severe damage of the upper surface layer can be seen, and the spongy structure was much more visible.

3.1.3 BET adsorption isotherm and pore analysis of biochar

The adsorption properties and capabilities of biochars were investigated based on nitrogen sorption isotherms. Figure 3a illustrates the adsorption/desorption isotherms (BET) for the WD samples, while Fig. 4a depicts the same for the RS samples. Figures 3b, c, d, and 4b, c, d illustrate the outcomes of the BJH pore analysis. Figures 3b and 4b illustrate the correlation between pore volume and pore diameter. The curves in Figs. 3c and 4c are derived and illustrate the size range of pores, as well as which of them contribute the most to the total pore volume and total surface area, respectively. The difference curves represent the change in volume between two neighboring pore sizes, divided by the difference in diameter of those pores. Therefore, they exhibit a preference for small pores, as the volume change is divided by a relatively small number. This shortcoming is offset by the frequency curves (Figs. 3d and 4d), which employ a logarithmic division of the volume change by the pore diameter. BHJ pore analysis results are summarized in Table 1.

The shape of adsorption isotherm can provide preliminary qualitative information on the adsorption mechanism

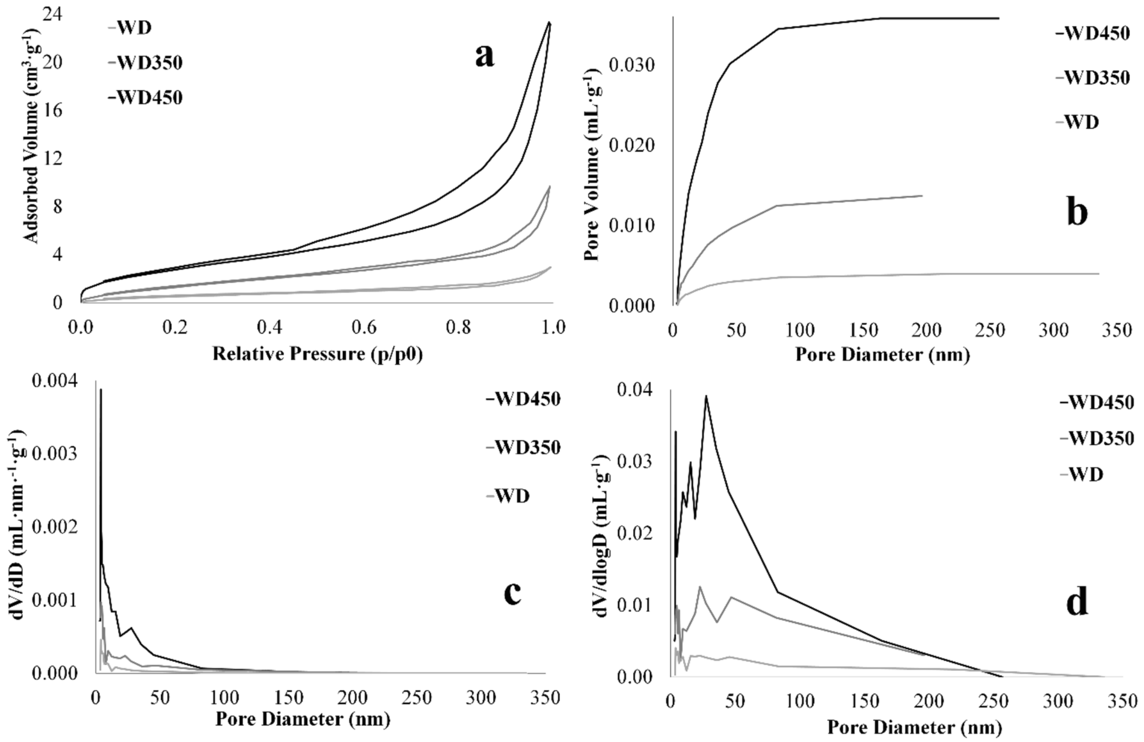


Fig. 3 WD biochars BET and BHJ pore analysis: **a** nitrogen adsorption/desorption isotherms; **b** pore size distribution, **c** difference curve, **d** frequency curve

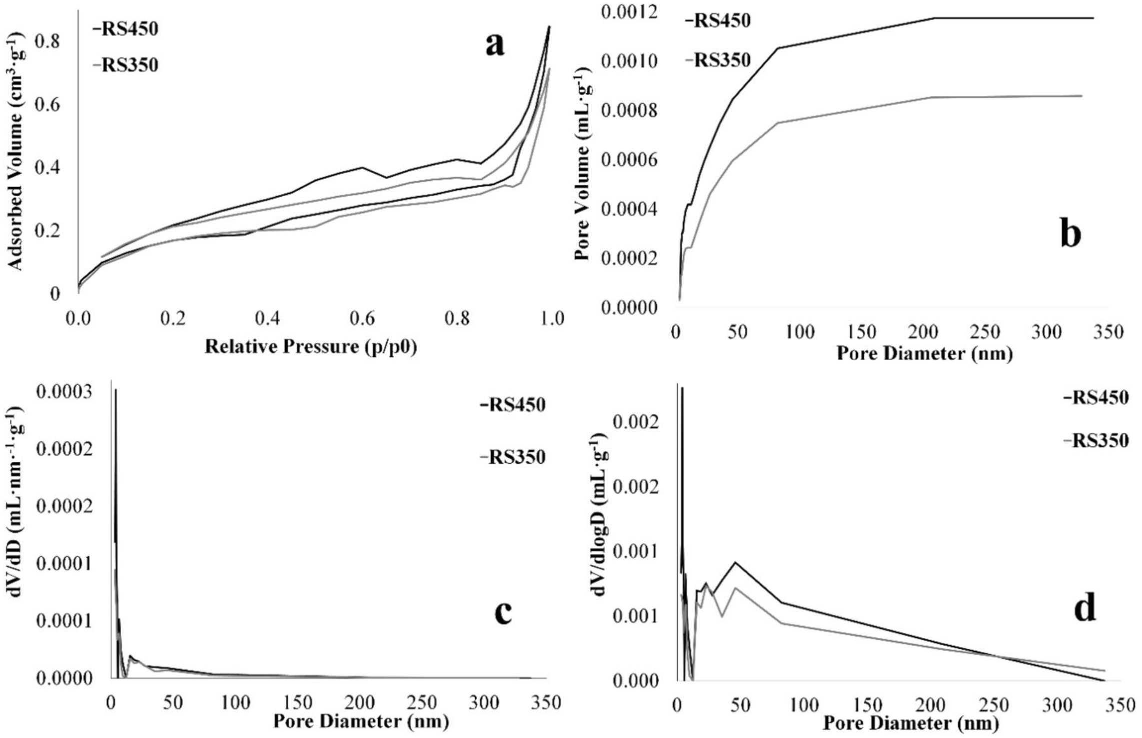


Fig. 4 RS biochars BET and BHJ pore analysis: **a** nitrogen adsorption/desorption isotherms; **b** pore size distribution, **c** difference curve, **d** frequency curve

Table 1 Summary of BJH pore analysis. Results are presented as minimum and maximum value and average of pore diameter, pore volume, and pore surface area for all tested samples

	Pore diameter (nm)			Pore volume (mm³·g⁻¹)			Pore surface area (m²·g⁻¹)		
	Min	Max	Average	Min	Max	Average	Min	Max	Average
WD	3.4	335	47.9	0.017	3.93	1.82	0.02	1.30	0.92
WD350	3.4	196	29.6	0.30	1.42	0.53	0.35	3.97	2.68
WD450	3.1	257	38.4	0.23	3.64	1.67	0.31	11.5	7.47
RS350	3.1	328	44.4	0.031	0.86	0.35	0.04	0.28	0.21
RS450	3.1	337	45.0	0.040	1.21	0.53	0.05	0.46	0.35

as well as on the porous structure of sample. All observed isotherms are IV type with H4 hysteresis loop, according to IUPAC classification. The isotherm type illustrates the simultaneous presence of micropores and mesopores in the structural composition of the analyzed samples [10]. As seen in Fig. 3a, the surface activation increased the adsorption capacity of the WD biochar. The SSA value was 2.2 $m^2 \cdot g^{-1}$ before activation. Activation at 350 °C resulted in a threefold increase in SSA, reaching 6.2 $m^2 \cdot g^{-1}$, and at 450 °C, the SSA exhibited a fivefold increase, reaching 11.0 $m^2 \cdot g^{-1}$. In the case of RS biochar sample (Fig. 4), the SSA was lower than the detection limit of the instrument (< 0.1 $m^2 \cdot g^{-1}$) and therefore BET and BHJ analysis could not be performed. Activation at 350 °C increased SSA to 0.7 $m^2 \cdot g^{-1}$ and at 450 °C to 0.8 $m^2 \cdot g^{-1}$.

The data summarized in Table 1 showed that the effect of the activation temperature played a significant role on the surface properties. In the case of WD, the activation resulted in a significant decrease in pore diameter, but an increase in their depth, which can be observed as an enlargement of the pore volume. The pore diameter remained unaffected in the RS sample. Only an increase in pore depth was observed at higher activation temperatures. Detailed BJH pore analysis revealed that all biochar samples had pores larger than 3 nm. According to the IUPAC definition, the size of micropores is less than 2 nm. The type of BET isotherm indicated that micropores would also be presented in the samples, but BJH analysis did not confirm this. The most contained pores in the samples had a diameter from 5 to 50 nm for WD and from 3 to 25 nm to RS biochar. As illustrated in Figs. 3b, c, d and 4b, c, d, the activation process resulted in a significant expansion of the these mesopores. This increase was observed to be directly proportional to the rise in activation temperature.

3.2 Biochar elemental analysis

Considering that the biochars were prepared from various waste biomasses, different elemental composition is expected. An extensive elemental analysis was performed on the tested samples (Table S1, Supplementary Files).

The carbon and nitrogen concentrations stay preserved in the biochars even after activation (Table S1, Supplementary Files). The concentration of hydrogen decreased due to activation. In the case of RS sample, by activation, the sulfur content was reduced, probably due to loss of volatile forms. For all other measured elements, in contrary, element concentrations increased proportionally with the activation temperature. The activation temperature was higher than the pyrolysis temperature, so it can be assumed that the biomass was not fully decomposed after pyrolysis and finally decomposed by activation. Volatile compounds also evaporated by higher activation temperature, so therefore elements became even more concentrated, up to twice after 450 °C activation. Nitrogen, calcium, magnesium, phosphorus, manganese, sulfur, sodium, and zinc contents were higher for RS compared to WD biochar. A comparison is presented in detail on Fig. 5. These elements are especially important for plants, such as macro- and micronutrients and biogenic elements. On the other hand, WD biochar contains much more aluminum and iron than RS biochar. The content of boron, barium, copper, and strontium is comparable. The measured mercury concentrations were below the limit of quantification (LOQ), which was 0.2 mg·kg^{-1} wt. The concentrations of these elements were below the LOQ of the used method in all samples: < 5 mg·kg^{-1} wt. for As, Bi, Li, Mo, Ni, Pb, Se, and < 2 mg·kg^{-1} wt. for Be, Cd, Co, Cr, and V.

3.3 Basic physico-chemical properties

Basic physicochemical properties such as pH value and CEC (Table 2) were determined in biochar samples. For utilization as a soil amendment, it is not necessary to activate its surface; therefore, these analyses were done only for raw biochars.

The results show (Table 2) that the CEC value is twice as high for RS biochar, which is consistent with the significantly higher total concentrations of total elements in the biochar (Table S1, Supporting Information). The pH values (Table 2) of both studied biochars were neutral, indicating that their application in the environment will not affect the pH value of water or soil.

Table 2 pH and CEC values of WD and RS biochars. Data are presented as an average ($n=2$) ± SD for CEC and average ($n=2$) ± 10% for pH

		WD	RS
CEC	[cmol·kg^{-1}]	43.1 ± 6.2	87.0 ± 8.5
pH	-	7.54 ± 0.08	7.04 ± 0.07

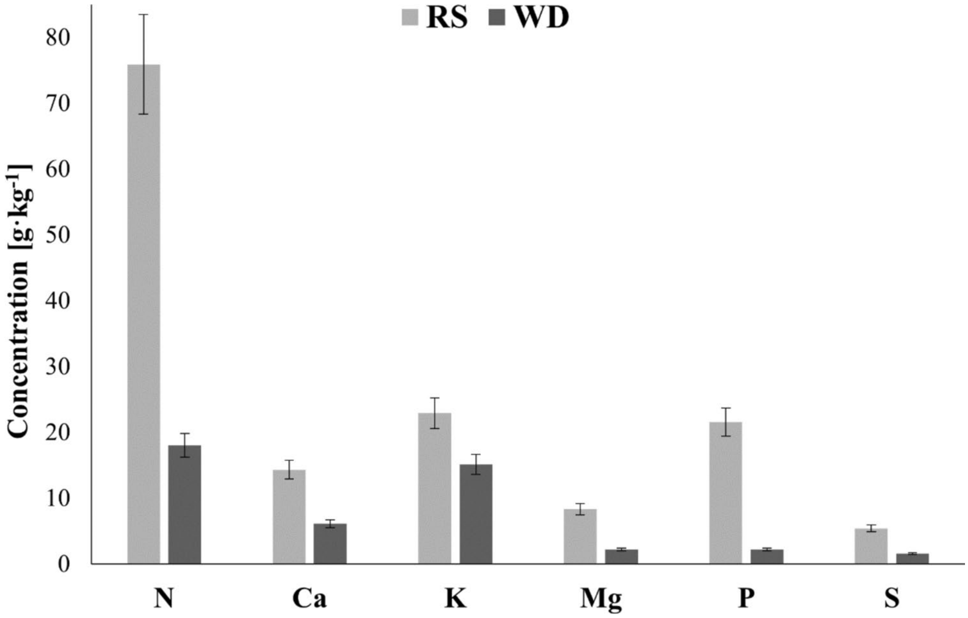


Fig. 5 Comparison of main nutrients concentrations in raw biochars; data are presented as an average ($n=3$) ± 10% RSD

4 Discussion

Subsequent appropriate and safe application of biochar can be suggested based on extensive composition, properties, and surface characterization. The properties and composition of the biochars are given by the raw material that was processed and the pyrolysis conditions. The latter primarily impacts the biochar properties, including pH value, structure, surface area, and functional groups bonded to it [39]. The raw material on the other hand has greater influence on the biochar composition [40]. In this work, the most frequent applications of biochar were assessed, namely soil amendment and adsorbent for pollutants removal from environment.

4.1 Evaluation of biochars utilization as an adsorbent

Various functional groups bonded to the biochar surface making it heterogeneous. In addition, the heterogeneity of biochar surface exhibits hydrophilic or hydrophobic properties. Bonded functional groups play a significant role in the adsorption process, because they determine the resulting polarity of the surface tension. Surface polarity and aromaticity of biochar are crucial factors of the adsorption process. Less polar and more aromatic biochars showed higher adsorption efficiency to organic pollutants in water treatment [36]. Specifically, the extent of aromatics and oxygenated functional groups in biochar could effectively bind to soil pollutants [41]. Upon exposure to O_2 and water during adsorption, the surface of biochar gets oxidized and forms more carboxylic and phenolic groups, and thus becomes hydrophilic. The results obtained by ATR-FTIR demonstrated differences in the type and concentration of functional groups bonded on surface (mainly aromatics and oxygenated), which may affect the capacity and mechanism of adsorption. The RS biochar had fewer functional groups compared to WS biochar. It is assumed that after steam activation, the composition of the functional groups will not change as in the case of chemical activation. The concentration of these functional groups increased with the higher activation temperature used, which agrees with similar published study [42]. Based on the H/C and O/C ratios obtained (Table S1, Supplementary Files), it is apparent that both biochars were equally aromatic. However, the WD biochar had a higher concentration of oxygenated compounds, making it more polar and hydrophobic than the RS biochar, and predicted high adsorption efficiency for organic pollutants.

Surface heterogeneity also exhibits the acidic/basic properties of biochar. The pH value is a critical parameter in the context of adsorption processes, as it exerts a profound influence on the efficiency and the underlying mechanism. It affects not only the adsorbent surface charge, but also the degree of ionization and speciation of the adsorbate [43]. At low pH value, most of these functional groups bonded on biochar surface are protonated and presented in positively charged form, thus favoring adsorption of the anions [44]. The surface of biochar is negatively charged in higher pH range, so that the cations can be easily captured by biochar surface. The pH value was neutral for both tested biochars, so the resulting pH of the soil or water will not be affected in case of applying the biochar as adsorbent. Due to the neutral pH, it is impossible to estimate whether they will be more effective for cations or anions.

The H/C and O/C ratios are used as basic predictors of the characteristics of biochar. A lower H/C ratio indicates a greater degree of carbonization and increased aromaticity, whereas higher O/C ratio indicates an elevated proportion of bound oxygen groups, resulting in a more hydrophobic and polar biochar [45]. Elevated H/C ratio was proved to be associated with enhanced adsorption efficiency of organic substances [46]. Furthermore, the aromaticity of biochar affects its absorption mechanism. It can be assumed that a higher H/C ratio results in a strong chemical bonding and high adsorption efficiency of organic substances for both tested biochars during the adsorption process [47].

Another important factor for the adsorption process is the biochar surface. In examining the structure of biochar, it was observed that a honeycomb structure was present in the WD biochar sample. This type of structure indicates good possibility for the dyes to be adsorbed [48]. In RS biochar, a spongy structure was detected, hidden under an upper layer. The activation caused the destruction of biochar surface as an effect of further devolatilization. The level of devolatilization has a considerable influence on the biochar characteristics. As known, the volatile matter release contributes to decreasing the biochar density and increasing the porosity [49]. A biochar with considerable destroyed surface could promote infiltration into the porous structure. In the RS biochar sample case, it would be necessary to choose a more aggressive method of surface activation to completely break the upper surface layer to improve the biochar sorption potentials.

Higher porosity helps improving the sorption properties of biochars through the facilitation of pollutants into the carbon matrix [50]. The suggestion is that micropores and small mesopores (2–20 nm) have a substantial influence on the biochar adsorption efficiency to organic compounds via pore-filling mechanisms [51]. For both tested biochar samples, the activation process improved the adsorption capacities of surface in correlation with the activation temperature raise. This can be considered an effect of the evolution of volatile matters out of the biomass matrix by increasing temperature [52]. The activation resulted in a decrease in pore diameter, but an increase in their depth, which can be observed as an enlargement of the pore volume. Activation caused an increase in the amount of mesopores. Consequently, RS biochar prepared under the given pyrolysis conditions is not a suitable adsorption material, because the resulting SSA is incredibly low even after activation. On the other hand, WD biochar with sufficient SSA value, pore surface area, and amount of mesopores and pore volume increasing even after activation seems to be a promising adsorption material.

4.2 Evaluation of biochars utilization as a soil amendment

From the point of view of using biochar as a soil amendment, its nutrient content is firmly important. Biochar will not only return these elements to the soil, but also reduce their leaching. In the case of carbon, its biological sequestration will take place. The main components as C, H, N, and O have different values in biochars [53]. In addition, the content of minor elements such as alkali metals and non-metals varies greatly in biochars depending on the raw biomass [54]. The tested samples contained a high concentration of carbon, which could lead to desirable sequestration to the soil. From the point of view of overall elemental composition, RS biochar seems to be a suitable material for utilization as a soil amendment. It contains many times higher concentration of main and micronutrients including trace elements than WD biochar. When comparing the nitrogen content in other types of biochar, the highest published nitrogen content found was reported as 7.30% wt. in microalgae biochar [55]. In this work, the nitrogen content was even 7.59% wt. in RS biochar. Moreover, 14.3 $g{\cdot}kg^{-1}$ wt. of calcium was determined in the RS sample. Similar concentration was reported in chlorella biochar [40] and in straw biochar [56]. In RS, 22.9 $g{\cdot}kg^{-1}$ wt. of potassium was detected. Analogous concentration was observed in grapevine biochar [57]. The highest magnesium concentration of 8.31 $g{\cdot}kg^{-1}$ wt. was displayed in RS, which is compared to the concentration published in switchgrass biochar [58]. RS biochar also recorded extremely high phosphorus content of 21.5 $g{\cdot}kg^{-1}$ wt., while the highest published phosphorus concentration found was 13 $g{\cdot}kg^{-1}$ wt. in corn stover biochar [59]. The sulfur content of RS biochar was determined to be 5.4 $g{\cdot}kg^{-1}$ wt., which is the closest match to the value of 3 $g{\cdot}kg^{-1}$ wt. observed in blackbutt wood biochar [60]. As can be seen from this comparison with worldwide characterized biochars originating from various sources, RS biochar contained exceedingly high concentrations of all macro- and micronutrients. In most of the tested biochar samples, high concentrations were limited to only one nutrient, in contrary to RS biochar that displayed elevated concentrations of multiple elements.

There are very few works dealing with comprehensive elemental analysis of produced biochars, including trace element determination. Especially the high content of risk elements can limit the use of biochar in agriculture. Both tested biochars contained concentrations of trace elements that meet the maximum acceptable limits, while all risk elements were below the limiting values in the decree 474/2000 coll. of the Ministry of Agriculture, Czech Republic and European Biochar Certificate—Guidelines for a Sustainable Production of Biochar [61, 62].

The pH value of biochars is quite variable and fluctuates from acidic to highly alkaline [63]. Soil pH is one of the most important soil parameters, as it affects most soil processes and has a stimulating or inhibiting effect on plant growth. The pH value also determines the ionic form and solubility of nutrients in the soil and thus their bioavailability to plants [64]. Addition of acidic biochar to the soil may result in unwanted acidification of the soil, or, conversely, the application of alkaline biochar may result in the desired neutralization of already acidic soil [65]. The neutral pH value of both tested biochars will not impact soil pH in case of applied as amendments.

CEC is often used to describe the fertility of soils. In the case of biochar, it indicates the availability of desirable alkaline elements in ranges usually from 5 to 50 $cmol{\cdot}kg^{-1}$ [65]. The application of biochar to soil results in the discharge of alkaline cations from the biochar, which then replace Al^{3+} and H^+ in the soil [66]. This results in an enhancement of the CEC of the soil. RS biochar exhibited a very high CEC value (87 $cmol{\cdot}kg^{-1}$) that was double that of the WD biochar, thus making it a considerably more suitable soil amendment.

In contact with water and oxygen in the soil, biochar exhibits increased hydrophilicity. The hydrophilic surface of biochar has been demonstrated to significantly enhance the CEC, nutrient retention capacity (NRT), and water holding capacity (WHC) of soil [67]. The hydrophilic surface of both tested biochar samples is beneficial for their intended soil application.

Having a large and porous surface, biochar can serve as a substrate for the growth of microorganisms. Its high content of carbon and other nutrients as well provides the microorganisms with the necessary nutrition [68]. From this point of view, WD biochar is more suitable based on higher porosity, despite that RS biochar also had certain porosity and surface which would also serve as a sufficient substrate.

4.3 Cost analysis

The estimation of the cost of biochar production from the raw materials tested is complicated by the fact that the final price is highly dependent on several currently unknown factors. According to published studies, the cost of producing a ton of biochar ranges from \$200 to \$2,000 [69]. This amount includes 30% attributed to the cost of the feedstock and its processing, 30–45% allocated to the pyrolysis process itself, and the remaining percentage allocated to storage, transportation, and packaging expenses [70].

The price of the input material, therefore, exerts a substantial influence on the total cost of biochar production. In the case of biomass grown directly for biochar production, it is necessary to include the costs of its processing, i.e., harvesting, cutting, chipping, transport, and storage. Conversely, when biowaste is purchased from the producer, these costs are not incorporated into the biochar production cost. However, the selling price of this input raw material must be considered. It is noteworthy to state that both waste biomasses examined in this study lack effective waste management systems and their subsequent sale is minimal. This is evident in the current selling price, which is consequently high. In the case of extracted rapeseed scrap, which is primarily utilized as animal feed, the price per ton is \$287. However, assumptions indicate that the price would be considerably lower if this raw material was purchased in bulk. Conversely, grain dust is a significantly more economical raw material, with a price of \$10 per ton.

A notable expense is the cost of pyrolysis, which includes the energy expended and the operational costs of the pyrolysis unit. This cost is influenced by various factors, including the type of pyrolysis unit used, its capacity, and the pyrolysis conditions. In our case, low-temperature pyrolysis was performed in a short time, which is an energy-saving process. It is noteworthy that both the tested biomass samples yielded approximately 77% biochar at the pyrolysis temperature used, which is an impressively high yield [71]. This high yield reduces the total costs necessary for biochar production. Another significant parameter in biomass processing via pyrolysis is its moisture content. In both cases, the biomasses exhibited a moisture content of 10%, thereby removing the necessity for pre-pyrolysis drying, which can significantly reduce processing costs.

The costs associated with material storage, transportation, and packaging are not yet available; however, for both biochars, these costs are considered fixed and can be expressed as a constant in the calculation of total costs, as they will remain constant for both.

This study examined two distinct biochars, with the cost of input material serving as the primary factor in determining their production costs. The findings and hypotheses can be outlined as follows: The cost of biochar derived from grain dust is projected to be at least \$100 per ton, while that of biochar derived from extracted rapeseed meal is estimated to be \$960 per ton, based on the current prices of the input raw materials. However, it is imperative to evaluate biochar's economic potential and value beyond its production costs. The price of biochar can be recalculated based on its carbon sequestration potential and nutrient content. Savings on the necessary additional fertilization can be considered as well. The application of more expensive biochar has the potential to yield greater benefits, including long-term cost savings or increased profits from crop harvesting. A comprehensive assessment of the pyrolysis process is essential, as it produces more than just biochar. The pyrolysis of biochars generates approximately 23% pyrolysis gas, a valuable fuel that can be utilized to heat the pyrolysis unit. The production of pyrolysis oil is also probable, constituting a highly valuable raw material. The effective and economic management of these pyrolysis by-products is likely to result in substantial cost savings in biochar production.

4.4 Future directions

To confirm the obtained conclusions, further work should deal with the verification of the effectiveness of WD biochar as an adsorbent for organic pollutants. Our newly published study [72] already confirmed that RS biochar is an effective soil amendment that returns nutrients to the soil and stimulates plant growth. Depending on this, our next goal is to carry out a life cycle assessment in order to bring the results obtained closer to the real application.

5 Conclusion

A significant amount of waste is generated during food processing, which presents a challenge in terms of its sustainable further processing. It is therefore necessary to identify new possibilities for transforming and utilizing this waste. In this study, the wheat dust and hexane-extracted rapeseed scrap were pyrolyzed and transformed into biochars, which can be used as a valuable new product. Furthermore, the biochar surface was activated by steam at two different temperatures (350 °C and 450 °C).

A satisfactory value of SSA ($11.0\ m^2 \cdot g^{-1}$) was determined for WD biochar upon activation at 450 °C. This sample also had sufficient porosity, structure, and composition of functional groups (aromatics and oxygenated) bonded on its surface, which predicted high adsorption efficiency. Due to its hydrophobicity, polarity, and aromaticity, the effective adsorption of organic substances could be expected, which will be supported by a high content of mesopores. The mean pore diameter after steam activation at 450 °C was 38.4 nm, while the mean pore volume was $1.67\ mm^3 \cdot g^{-1}$. Based on neutral pH value, it is impossible to estimate whether the biochar will be more suitable for cations or anions adsorption. It will probably be more universal for effective sorption of diverse types of pollutants. In addition, the pH of the water or soil will not be adversely affected during using biochar. Based on the obtained results, WD biochar can be recommended as propriety material for adsorption of organic pollutants (e.g., dyes, pesticides, pharmaceuticals) from environment. It is assumed that following the activation of the steam, the sorption capabilities will be enhanced.

Raw RS biochar elemental composition was more than suitable for utilization as a soil amendment. It contained exceedingly high levels of macro- and micronutrients (N 75.9 $g{\cdot}kg^{-1}$ wt., P 21.5 $g{\cdot}kg^{-1}$ wt., K 15.1 $g{\cdot}kg^{-1}$ wt., Ca 14.3 $g{\cdot}kg^{-1}$ wt., Mg 8.31 $g{\cdot}kg^{-1}$ wt., S 5.40 $g{\cdot}kg^{-1}$ wt.). All toxic and risk elements had a concentration below the limit that would make its application to the soil possible. Biochar has a neutral pH value and therefore will not significantly affect its value in the soil. The CEC value was also remarkably high (87.0 $cmol{\cdot}kg^{-1}$), so it can be assumed that soil fertility will increase after biochar application. Biochar's porosity and high carbon content (60.3 wt. %) will be beneficial for the growth and nutrition of soil microorganisms. Its use in agriculture would lead to the improvement of soil properties and especially to the return of nutrients back into the soil.

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Data availability Data will be available upon request.

Declarations

Consent for publication The manuscript adheres to the Ethics in Publishing Policy, and the all authors and relevant institutional authorities approved its publication.

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