

Article

High-Performance Concrete Nanomodified with Recycled Rice Straw Biochar

Alexey N. Beskopylny ^{1,*}, Sergey A. Stel'makh ², Evgenii M. Shcherban' ², Levon R. Mailyan ³, Besarion Meskhi ⁴, Alla S. Smolyanichenko ⁵ and Nikita Beskopylny ⁶

¹ Department of Transport Systems, Faculty of Roads and Transport Systems, Don State Technical University, 344003 Rostov-on-Don, Russia

² Department of Engineering Geology, Bases, and Foundations, Don State Technical University, 344003 Rostov-on-Don, Russia; sergej.stelmax@mail.ru (S.A.S.); au-geen@mail.ru (E.M.S.)

³ Department of Roads, Don State Technical University, 344003 Rostov-on-Don, Russia; lrm@aaanet.ru

⁴ Department of Life Safety and Environmental Protection, Faculty of Life Safety and Environmental Engineering, Don State Technical University, 344003 Rostov-on-Don, Russia; spu-02@donstu.ru

⁵ Department of Water Supply and Sewerage, Don State Technical University, 344003 Rostov-on-Don, Russia; arpis-2006@mail.ru

⁶ Department Hardware and Software Engineering, Don State Technical University, 344003 Rostov-on-Don, Russia; beskna@yandex.ru

* Correspondence: besk-an@yandex.ru; Tel.: +7-8632738454

Abstract: The development of new and improvement of existing technologies based on the use of waste products from various industries or recyclable materials is a current trend in the construction industry. Including in the composition of binders and concrete by-products of industry, reducing the proportion of Portland cement, it is crucial to maintain and improve the resulting products' mechanical characteristics and life cycle. The main aim of the study was to investigate the influence of biochar additive on the microstructure and properties of the concrete and obtain the composition with improved characteristics due to nanomodification of rice straw recycled biochar. An environmentally friendly technology for concrete manufacture was obtained, using agricultural waste, rice straw, as its components, developing a composition of concrete nanomodified with processed rice straw biochar, identifying the dependences of concrete properties on their nanomodification with processed rice straw coal. It has been established that the most effective dosage is the addition of rice straw biochar in the amount of 6% by weight of cement. The improvement in the properties of concrete was expressed in the increase in its physical and mechanical characteristics and changes in deformability according to the results of the analysis of the stress-strain diagrams. The increase in strength characteristics ranged from 17% to 25%. The modulus of elasticity increased to 14%. The deformation characteristics decreased from 12% to 24%. Introducing a finely dispersed additive of rice straw biochar modified by the electromagnetic method leads to a decrease in cement consumption by up to 10%.

Keywords: concrete; rice straw; biochar; nanomodification; strength characteristics; deformation characteristics

Citation: Beskopylny, A.N.; Stel'makh, S.A.; Shcherban', E.M.; Mailyan, L.R.; Meskhi, B.; Smolyanichenko, A.S.; Beskopylny, N. High-Performance Concrete Nanomodified with Recycled Rice Straw Biochar. *Appl. Sci.* **2022**, *12*, 5480. <https://doi.org/10.3390/app12115480>

Academic Editor: Carlos Thomas

Received: 15 May 2022

Accepted: 27 May 2022

Published: 28 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The current world resource-saving policy is based on creating new and developing current technologies, including the use of industrial waste in various directions or recyclables [1–3]. This trend is relevant to the construction industry, especially in creating composite building mixtures and concrete [4–6]. As a result, the global cement industry occupies one of the top areas after energy and transport in “greenhouse gas emissions” (5–8%) from the combustion of Portland cement clinker [7–9]. It should be noted that when the by-products of industry are included in the composition of binders and

concretes, thereby reducing the proportion of Portland cement, it is essential to both maintain and improve the mechanical characteristics and life cycle of the resulting products [10,11].

The required tasks can be achieved by introducing biologically based components into concrete, which, according to well-known scientific studies, “have a positive effect on the strength characteristics of concrete” [12,13]. It is possible to use carbonized biomass based on rice straw. At the same time, an urgent problem is the disposal of waste from the agro-industrial complex, including rice straw and rice husks [14,15]. The Russian Federation is a major producer of rice; in 2019, the harvest amounted to 1098.7 thousand tons. The leader in the cultivation of rice in Russia is the Krasnodar Territory (73.3%), the Republic of Dagestan is in second place (8.7%), followed by the Rostov Region (7.7%). It is known that from 1 ton of rice, on average, 1 ton of straw and 200 kg of husks are obtained. These wastes are among the least rotting wastes of the agro-industrial complex (AIC), but at the same time, they contribute to the spread of blast, a dangerous rice disease that leads to a 15–40% yield loss [16–18].

For the most part, farms solve this problem by burning straw, which also leads to several negative consequences. Firstly, the danger of landscape fires, and secondly, many toxic substances are released into the atmosphere in the burning area [19,20]. Thus, in order to solve such significant environmental problems as reducing CO₂ emissions and recycling agro-industrial complex, it is proposed to create an environmentally friendly technology for producing concrete nanomodified with processed rice straw biochar [20,21]. Biochar is a solid residue obtained from biomass by controlled thermal decomposition (pyrolysis) and gasification under conditions of limited oxygen access [22,23]. The defining parameters of the carbonization process are heating rate, temperature, feed rate, and residence time. Changing the above parameters and the quality of raw materials affects the resulting biochar's structure, chemical composition, and yield [24,25].

Biochar or biochar from agricultural waste—rice straw and rice husks—are environmentally friendly and inexpensive materials [26–28]. There are domestic standards for the production of biochar—GOST 7657-84 “Charcoal. Specifications” [29] and GOST 24260-80 “Wood raw material for pyrolysis and charring. Specifications” [30], which impose requirements on the quality of the feedstock in terms of its production, but not its safety in relation to human health. The European Biochar Quality Mandate sets a high ecological threshold for the chemical composition of biochar—BQM, the European Biochar certificate, according to which biochar is divided into a product of standard and high quality.

This conclusion can be drawn from the biochar research statistics of the world's main funding organizations: National Natural Science Foundation of China (NSFC) (23.8%), Fundamental Research Foundations for China Central Universities (3.2%), National Key Research and Development Program of China (3.14%), National Science Foundation (NSF) (2.78%), China National Basic Research Program (2.57%), United States Department of Agriculture (USDA) (2%), Chinese Academy of Sciences (1.95%), European Union (EU) (1.78%), China Scholarship Council (1.66%), Science and Engineering Research Council of Canada (1.64%) [31].

The production of biochar from waste wood and agriculture is carried out in BM-Engineering (Kyiv, Ukraine), Pyropower (Ede, The Netherlands). In Norway, the R&D program—VOW (Turning Organic Waste into Environmentally Friendly Products for Cleaning Polluted Water, Soil and Air)—is conducting research on the possibilities of biochar, the purpose of which is to use biological waste to create sustainable products for cleaning soil, air, and wastewater [32].

Rice husk ash is used as pozzolan, which is a finely dispersed material that, in the presence of water, reacts with calcium hydroxide released during the hydration of Portland cement to form calcium silicate hydrate and other binders [10]. Different options for using rice husk ash as a pozzolan and a cement component were considered in [11]

and [12]. When rice husks are burned “below the silica crystallization temperature, ash is formed, which has a predominantly amorphous character” [13,14] with its reactivity due mainly to “the inner surface of microporous particles. Quickly cooled ash has the maximum amount of silanol groups, which are important for the pozzolanic additive in cement” [15], and the pozzolanic activity increases during grinding [16]. The setting of concrete increases with “increasing ash content, and when used in masonry concrete, rice husk ash provides good strength and durability” [17].

In addition, the inclusion of 20–30% rice husk ash improves resistance to sulfates, acids, and chlorides [13], “while 20% Portland cement can be replaced with rice husk ash without adversely affecting its strength” [18]. The water requirement for rice husk ash when used as a partial replacement for cement can be controlled by mixing with clinker during cement production or by mixing it with cement at the point of use. Rice husk ash fixes free lime released during the hydration of clinker silicates, and amorphous silica reacts with $\text{Ca}(\text{OH})_2$ in a secondary hydration reaction to form a porous structure with a large specific surface area, which increases the strength and durability of concrete” [19].

The possibility of using rice husk ash in recycled concrete aggregate (RCA) is considered in [33,34]. Compared to other additives, rice husk ash has shown superior performance in terms of the mechanical properties of RCA [33]. In addition, rice hull ash can be used as a partial replacement for cement to mitigate the poor performance of RCA concrete and improve the bond between concrete and fibers [34].

Works [35–38] are devoted to the issue of using various types of waste. The effect of compaction state and dry-wet cycles on crack propagation in biochar soils was examined by performing multiple regression analysis and developing a multiple regression model to estimate crack intensity in biochar soils based on soil and biochar properties. Woody biochar had a higher resistance to crack propagation compared to hog manure biochar. The proposed method provided preliminary qualitative information about the intensity of cracks in the samples when the main properties of the soil are known [35]. The use of cellulose fiber as a reinforcing material in polymer matrices is considered in [36]. Composites reinforced with cellulose fiber are sufficiently strong, light, harmless to human health and the environment, and biodegradable, so they can be used in various fields as structural components of cars, aerospace structures, structures, etc. Aspects of fiber processing to improve the mechanical properties of composites, production methods, characteristics of hybrid composites, the effect of laminate configuration, and many different applications of natural fiber composites are highlighted [36]. The creation of ecological materials from green resources based on nanocellulose materials is considered in [37]. Cellulosic nanomaterials have environmentally sustainable characteristics such as biodegradability, biocompatibility, and potential availability in abundance at a lower cost. The various sources of cellulose fiber extraction and their methods, the purification processes used, the various sample preparation and drying methods for cellulose nanomaterials, and the methods used to closely study cellulose nanocrystals and nanofibers when used in polymer matrix composites are discussed. The advantages of using cellulose nanomaterials in the paper, oil and gas industries, food packaging, medical and printed electronic fields are highlighted [37]. Nanofillers help improve various properties such as mechanical, thermal, flame retardant, and water-absorbent properties of nanocomposite materials, as well as maintain their optimum density. The use of nanocomposites is quite effective due to their large surface area, aspect ratio, and excellent properties [38].

This investigation is based on developing a concept of “green concrete”, which consists of the partial replacement of cement in concrete composition with rice straw carbonization. The carbonization is additionally subjected to electromagnetic treatment to create the effect of magnetic susceptibility, improve the strength characteristics of concrete, and reduce its water demand. It is planned to impart the properties of magneto sensitivity and increase the strength characteristics by processing the concrete mixture in an electromagnetic installation, which can ensure uniform mixing of the mixture

components in an electromagnetic field and allow water-reducing additives to be evenly applied to the processed components.

The article's main aim is to investigate the influence of biochar additive on the microstructure and properties of the concrete and obtain the composition with improved characteristics due to nanomodification of rice straw recycled biochar.

The scientific novelty of the research lies in:

- (a) Theoretical and experimental verification of the compatibility of a nanomodifier aggregate of plant origin, namely, processed rice straw coal with the mineral components of concrete—Portland cement, inert aggregates—crushed stone and sand, and the establishment of rational qualitative and quantitative parameters that ensure the best compatibility;
- (b) Identification of the main factors influencing the processes of structure formation and the formation of properties of the obtained stone materials based on agricultural waste;
- (c) Analytical, mathematical, and structural-physical substantiating characteristics, understanding, and representation of the processes occurring during the formation of structures and the formation of properties at the micro and macro levels of such nanomodified concretes;
- (d) Revealing the dependence of the properties of concretes on their nanomodification with processed rice straw coal, obtaining new knowledge about the formation of the quality of such concretes, developing existing theoretical and practical ideas about the effect of nanomodification with processed rice straw biochar on the properties of cement-based concretes, and determining the role of such modification in the formation of final properties of concrete.

2. Materials and Methods

In the experiments, Portland cement of the CEM I 42.5N brand produced by JSC Novoroscement (Novorossiysk, Russia) was used. Table 1 presents the main physical and mechanical properties of Portland cement, and Table 2 shows its mineralogical and chemical composition.

Table 1. Physical and mechanical characteristics of Portland cement.

Indicator	Value
Residue on a 45 µm sieve, %	3.5
Blaine specific surface area, cm ² /g	3635
Normal density of cement paste, %	27.7
Beginning of setting, min	138
End of setting, min	187
Compressive strength at the age of 28 days, MPa	52.2
Flexural strength at the age of 28 days, MPa	8.5
Uniformity of volume change, mm	0

Table 2. Mineralogical and chemical composition of Portland cement.

Mineralogical Composition, %				Chemical Composition, %					
C ₃ S	C ₂ S	C ₃ A	C ₄ AF	MgO	SO ₃	Na ₂ O + K ₂ O	CaO	SiO ₂	LOI
68.8	10.3	8.9	11.3	0.9	2.34	0.75	50.1	14.0	3.56

Granite crushed stone produced by Pavlovsk Nerud JSC (Pavlovsk, Russia) was used as a large dense aggregate, with the following physical and mechanical characteristics: fraction size—5–20 mm; bulk density—1503 kg/m³; true density—2620 kg/m³; crushability—11.4% by weight; the content of lamellar (flaky) and acicular grains is 8.1% by weight; voidness—43%.

Quartz sand produced by OAO Arkhipovsky Quarry (village Arkhipovskoye, Belorechensky District, Krasnodar Territory, Russia) with the following physical characteristics was used as a fine aggregate: fineness modulus—1.66; the content of dust and clay particles is 1.2%; bulk density—1438 kg/m³; true density—2650 kg/m³.

Recycled rice straw biochar modified by the electromagnetic method was used as a modifying additive. The method for obtaining rice straw carbonization (rice husk) is shown in Figure 1.

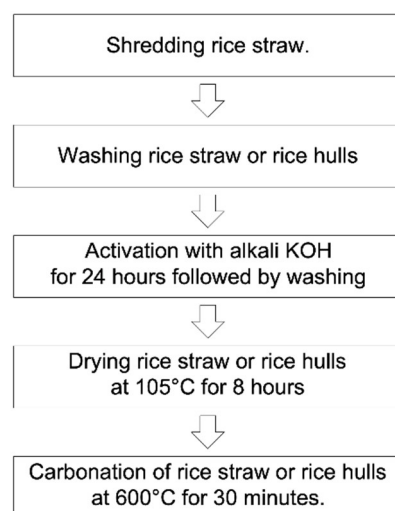


Figure 1. Method for obtaining carbonized rice straw (rice husk).

Potassium hydroxide (KOH) produced by Soda-chlorat LLC (Berezniki, Russia) was used to activate rice straw. The alkali solution concentration was 20 g per 1 L of water (2% KOH solution).

For drying at a temperature of 105 °C to obtain rice straw carbonization, an ShS-80-01 SPU drying oven (Smolensk SKTB SPU, Smolensk, Russia) was used. Carbonization of rice straw was carried out in a laboratory electric furnace SNOL 6.7/1300 (AB UMEGA GROUP, Utena, Lithuania).

Electron microscopy and simultaneous thermal analysis were also performed for the obtained sample of rice straw biochar modified by the electromagnetic method.

The microstructure was studied using a ZEISS CrossBeam 340 (Carl Zeiss Microscopy GmbH (Factory), Jena, Germany).

Synchronous thermal analysis was performed on a STA 449 F1 Jupiter instrument (NETZSCH-Gerätebau GmbH, Selb, Germany). Thermal analysis was carried out in the air.

Electromagnetic treatment was carried out on a process activation unit (UAP) manufactured by DSTU (Rostov-on-Don, Russia). With small equipment sizes and low unit energy costs, UAP allows changing the structure and properties of processed materials. The scheme of the process activation installation is shown in Figure 2, and the general view of the UAP (Figure 3a), the working body (Figure 3b), and the control cabinet (Figure 3c), as well as the side view of the loading opening (Figure 3d) are shown in Figure 3.

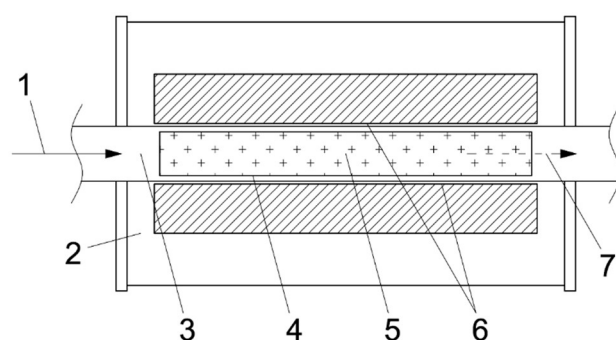
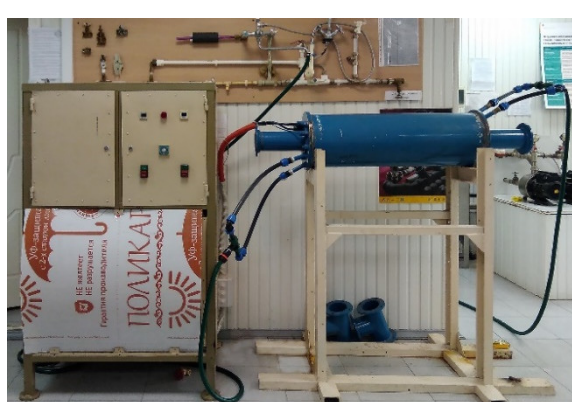
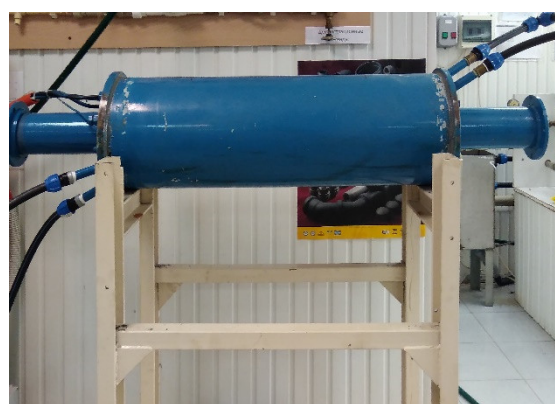


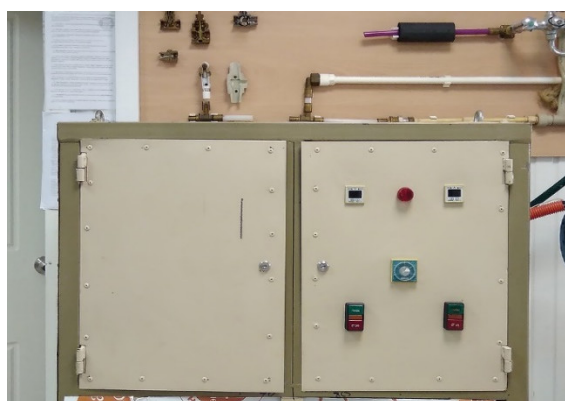
Figure 2. Scheme of the process activation installation: 1—incoming liquid flow for processing; 2—cooling jacket housing; 3—working area; 4—replaceable insert; 5—working bodies—ferromagnets (needles); 6—induction coils; 7—processed stream.



(a)



(b)



(c)



(d)

Figure 3. Photo of the process activation unit: (a) general view; (b) working building; (c) control cabinet; (d) side view of the working body, feed opening.

The principle of operation of the UAP is as follows: when voltage is applied to the windings of the induction coils (6), a powerful rotating electromagnetic field is created inside the cavity of the pipe (3), which rotates the ferromagnetic elements (5).

The needles (5), under the influence of a powerful electromagnetic field, due to their ferromagnetic properties, interact with the main rotating field, at the same time creating their own local fields.

As a result of this interaction, a number of effects are generated in the working space (including the magnetostrictive effect and the cavitation effect), which strongly influence

the change in the properties of the processed materials passing through the processing zone (3) of the UAP.

The working bodies in the working space are ferromagnetic particles, which are pieces of wire made of iron (steel) or nickel, which are commonly called needles. According to [39,40], when needles enter a volume affected by a field, they themselves become magnets or dipoles and are magnetized to saturation.

Concrete mixes were prepared in a laboratory forced-action concrete mixer BL-10 (OOO ZZBO, Zlatoust, Chelyabinsk region, Russia). To compact the mixtures in the process of molding the samples, a standard laboratory vibration platform SMZh-539-220A (LLC IMASH, Armavir, Russia) was used, and the vibration time was 60 s.

The process of hardening concrete samples is one of the essential technological stages. During this period, the structure of the cement stone is formed. Heat and moisture treatment was carried out in the KUP-1 steaming chamber (RNPO RusPribor LLC, Chelyabinsk, Russia) at an isothermal holding temperature of 80 °C, following next characteristics:

- Temperature rising for 3 h;
- Isothermal exposure for 6 h;
- Cooling in a closed chamber for 15 h.

After that, the samples were kept in natural air conditions for 14 days.

The sample preparation procedure included the following steps:

- (1) At the dosing stage, VLTE-2100 scales (NPP Gosmetr, St. Petersburg, Russia) were used with an accuracy of 0.05 g to measure the required mass of concrete components;
- (2) At the stage of loading into the concrete mixer, the sequence was as follows: water, cement, additive, sand, crushed stone;
- (3) Then, the stage of mixing the components in a concrete mixer was carried out until homogenization and obtaining a homogeneous consistency of the mass;
- (4) After homogenization, the mixture was unloaded into sample molds, which were subsequently installed on a laboratory vibration platform and compacted to the required state;
- (5) After compaction, the samples were placed in a steaming chamber for 1 day, and then, after demoulding, they were kept in natural air conditions for 14 days;
- (6) Further, the samples were tested on the IP-1000 hydraulic press (NPK TEHMASH LLC, Neftekamsk, Republic of Bashkortostan, Russia) and R-50 tensile testing machine (IMASH LLC, Armavir, Russia) in accordance with the requirements GOST 10180 "Concretes. Methods for strength determination using reference specimens" [41] and GOST 24452 "Concretes. Methods of prismatic, compressive strength, modulus of elasticity and Poisson's ratio determination" [42];
- (7) Control and strength of concrete assessment was carried out in accordance with GOST 18105-2018 "Concretes. Rules for control and assessment of strength" [43].

Six series of samples were made and tested with different dosages of rice straw biochar modified by the electromagnetic method. The experimental research program is shown in Figure 4.

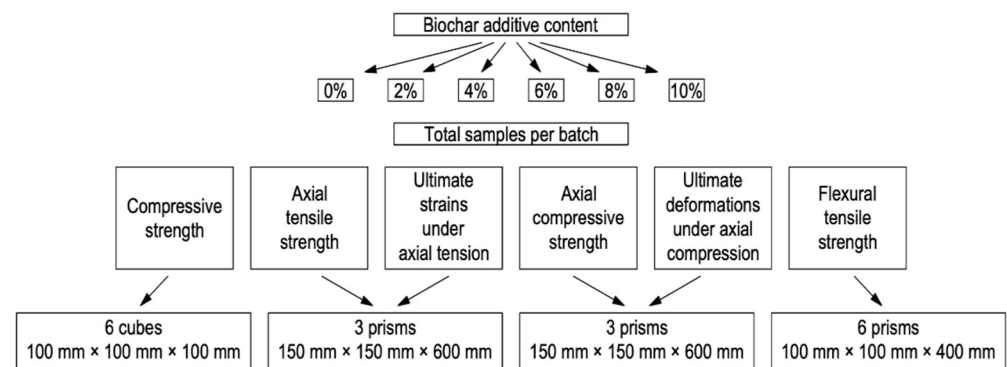


Figure 4. The program of experimental studies on the effect of dosage of rice straw biochar on the strength and deformation characteristics of concrete.

During the research, standard methods for testing raw materials and prototypes based on them were used.

Flexural compressive and tensile strength tests were carried out in accordance with GOST 10180 “Concretes. Methods for strength determination using reference specimens” [41].

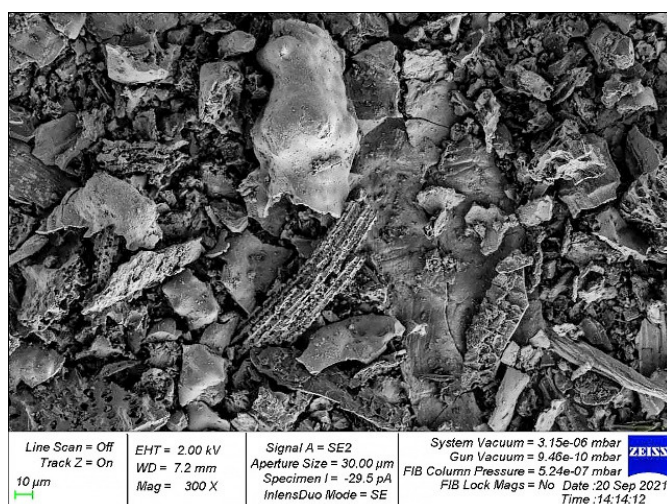
Determination of prismatic strength was carried out in accordance with the requirements of GOST 24452 “Concretes. Methods of prismatic, compressive strength, modulus of elasticity and Poisson’s ratio determination” [42].

In addition, in this study, “measuring instruments were used (NPO LABORKOMPLEKT, Moscow, Russia): metal measuring ruler 500 mm; device for measuring deviations from the plane NPL-1; device for measuring deviations from perpendicularity NPR-1” [44–47].

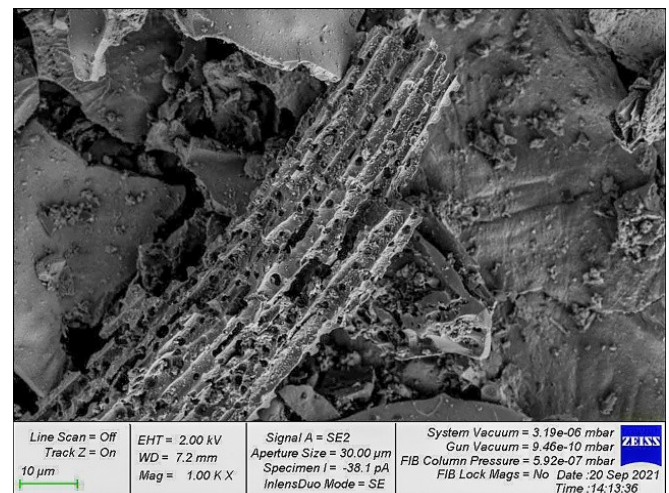
3. Results

3.1. Evaluation of the Microstructure and Chemical Composition of Rice Straw Biochar

Based on the results of SEM, photographs of the microstructure of biochar samples of rice straw modified by the electromagnetic method were obtained, which are shown in Figure 5.



(a)



(b)

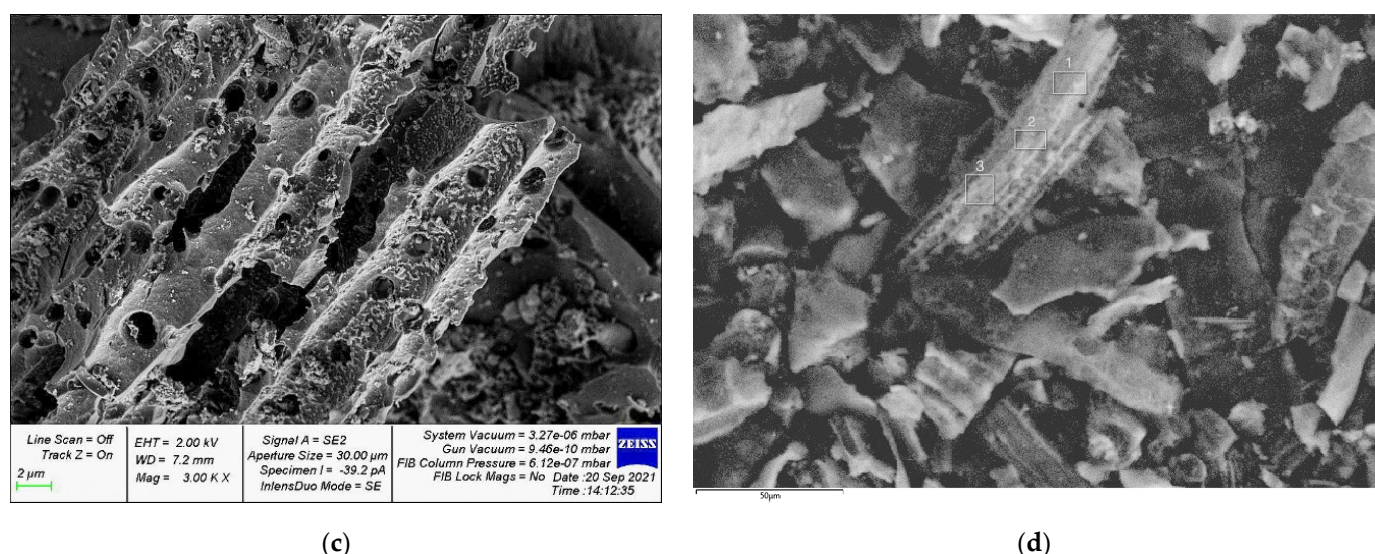


Figure 5. Microstructure photo of rice straw biochar samples: (a) with a resolution of 10 nm, (b) with a resolution of 3 nm; (c) with a resolution of 1 nm; (d) regions 1, 2, 3 selected for EDX spectroscopy.

A sample of rice straw biochar is a corpuscular porous body, and individual particles of which have ordered cylindrical pores without a bottom of approximately equal size. The material itself can be directly attributed to nanomaterials with a particle size of 10 to 100 nm.

The electromagnetic activation method makes it possible to obtain a mesoporous-type nanomaterial from APC waste with a modified surface structure of particles, which can intensify the process of mixing concrete with water. This material optimizes the curing cycle of concrete by reducing the curing time and increasing the class of concrete. In addition, a significant advantage of using an electromagnetically activated additive from rice straw biochar is the long-term absence of microcracks during the operation of a concrete structure due to the homogeneity of the concrete body and the reinforcing effect of biochar.

Figure 6 shows the EDX spectrum of a rice straw biochar sample.

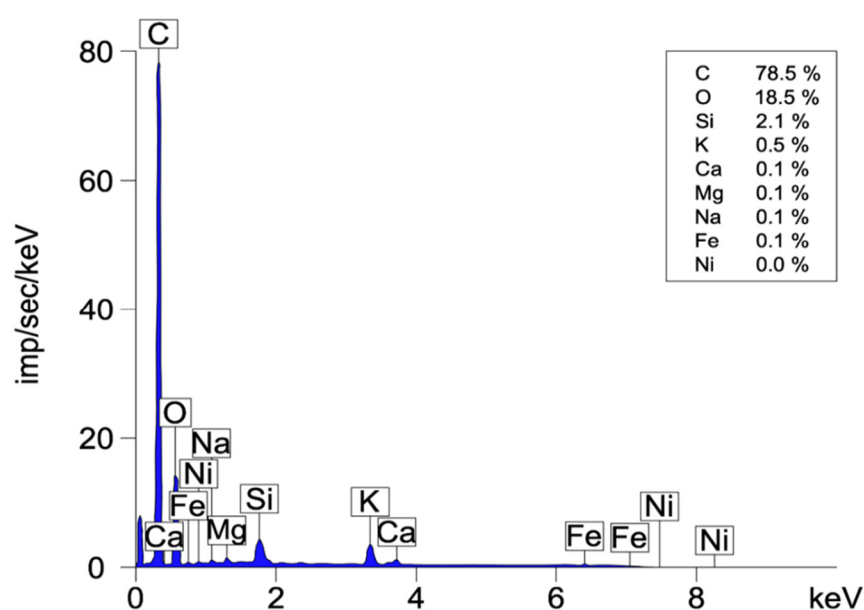


Figure 6. EDX spectrum of rice straw biochar samples.

The EDX spectrum covers the presence of C, O, Si, K, Ca, Mg, Na, and Fe in the biochar sample. As can be seen from Figure 6, the chemical composition of the obtained biochar is mainly represented by carbon, the content of which is 78.5%. In addition, the EDX spectrum of the biochar sample shows a small amount of Fe. The presence of iron in the chemical composition of biochar can be explained by its electromagnetic activation carried out at the UAP installation.

The sample analysis result—rice straw magnetostriktion—is shown in Figure 7.

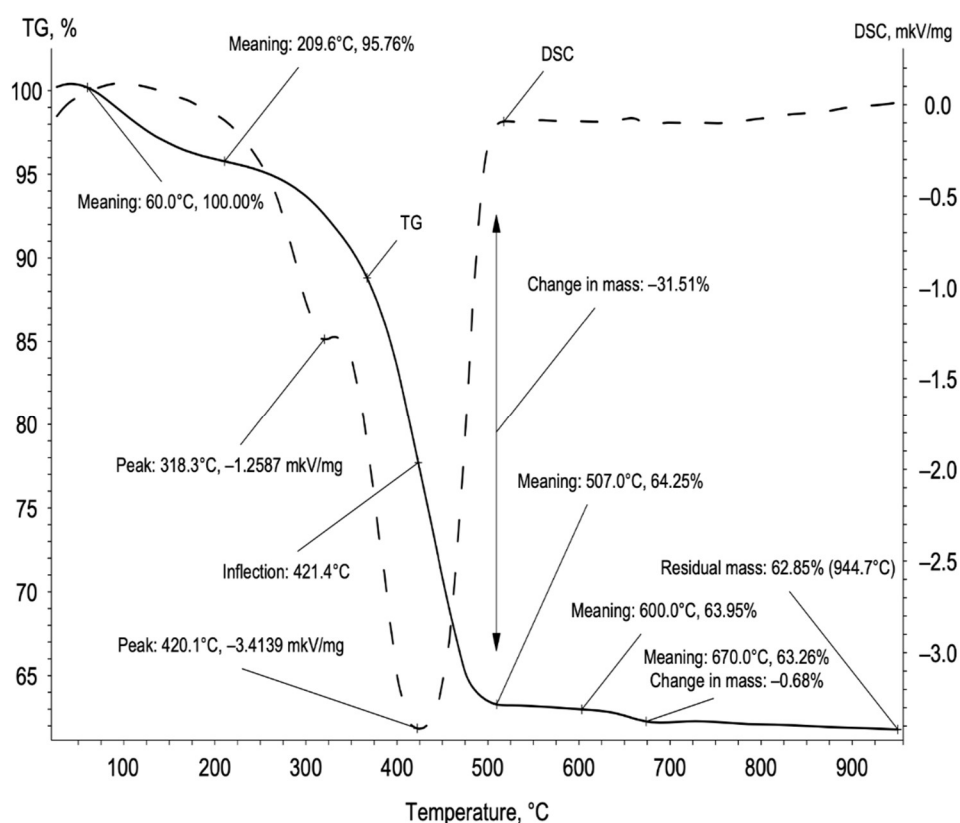


Figure 7. Results of thermogravimetric analysis of a sample of rice straw biochar modified by the electromagnetic method: TG—thermogravimetry, obtained by determining the mass loss during heating to high temperatures; DSC—differential scanning calorimetry.

Weight loss begins at temperatures above 60 °C and is 4.2% in the range from 60 °C to 210 °C; further weight loss is more intense. The interval 210–510 °C is accompanied by a loss of 27% of the mass with a complex exothermic effect with maxima at 318 °C and 420 °C. In this interval, the decomposition and release of organic substances and the combustion of combustible material probably occur.

In the range of 600–670 °C, a loss of 0.68% of the mass is observed, probably, to the release of chemically bound moisture, as well as a certain amount of organic volatile substances.

Residual mass at 950 °C is 62.85%. At the same time, after 670 °C, the rate of weight loss is noticeably reduced, which may indicate a possible imminent end of the decomposition process.

3.2. Phenomenological Model of the Influence of the Dosage of Rice Straw Biochar Addition on the Strength and Deformation Characteristics of Heavy Concrete

An analysis of the effect of a nanomodifying additive on the strength properties of concrete shows that the additive generates physical and chemical processes that can be conditionally divided into constructive, that is, increasing strength, and destructive, reducing strength. A slight increase in strength is observed with a small amount of

nanomodifying additive. Too much amount leads to a decrease in strength. These processes develop in parallel and have a phase shift, as a result of which the dependence of the strength characteristic Y on the amount of nanomodified additive X has the form:

$$Y = C_0 + Ax^b \sin(\omega x + \varphi), \quad (1)$$

where C_0 is the value of the strength characteristic without additive; A, b, ω — constants that determine the kinetics of strength changes; φ — phase.

The theoretical substantiation of the observed effect is as follows. When the additive is introduced in the optimal amount, it becomes the crystallization center for the emerging concrete microstructure, and at the same time, the structure has the densest packing of particles and, accordingly, the best mechanical and deformation characteristics, which can improve the operational reliability of the resulting concrete.

When the amount of the nanomodifying additive is exceeded in excess of the optimal amount, the effect of insufficient wetting of the surface of the binder particles occurs, the phenomenon of increased water demand and insufficient hydration of the cement occurs, thereby the finely dispersed nanomodifying additive has a harmful, destructive effect on the emerging structure of the building composite-concrete. That is, we obtain a model when, with an increase in the content and saturation of the concrete mix with a nanomodifier, with a simultaneous increase in indicators (that is, a constructive effect), there is a simultaneous destructive effect, thereby confirming the validity of the proposed dependence.

Consider the application of function (1) to the problem under consideration.

As a control composition, heavy concrete of class B30 with the required grade for workability P1 (cone draft 1–4 cm) was designed. The parameters of the composition of the concrete mixture obtained as a result of the calculations are shown in Table 3.

Table 3. Parameters of the composition of the concrete mixture.

Indicator Title	Cement, kg/m ³	Water, l/m ³	Crushed Stone, kg/m ³	Sand, kg/m ³	ρ_{cm} , kg/m ³
Indicator value	375	210	1028	701	2314

The results of experimental studies of the influence of the dosage of rice straw biochar on the strength characteristics of heavy concrete are presented in Figures 8–11.

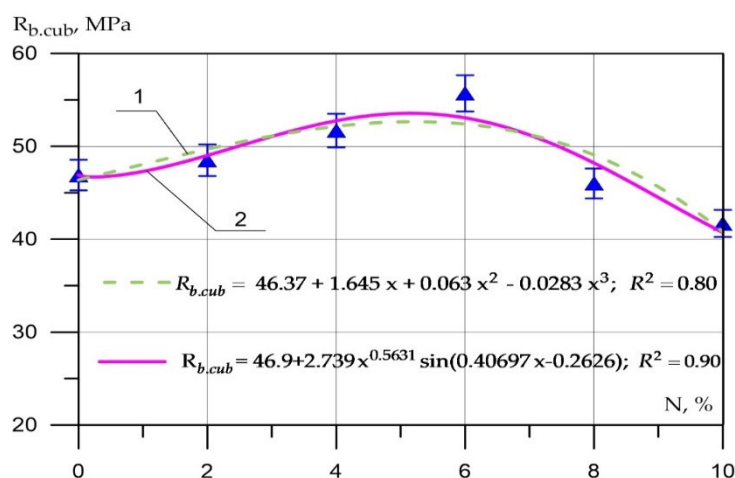


Figure 8. Results of experimental studies of the effect of dosage of rice straw biochar on compressive strength: 1—polynomial of the 3rd degree; 2—function (1).

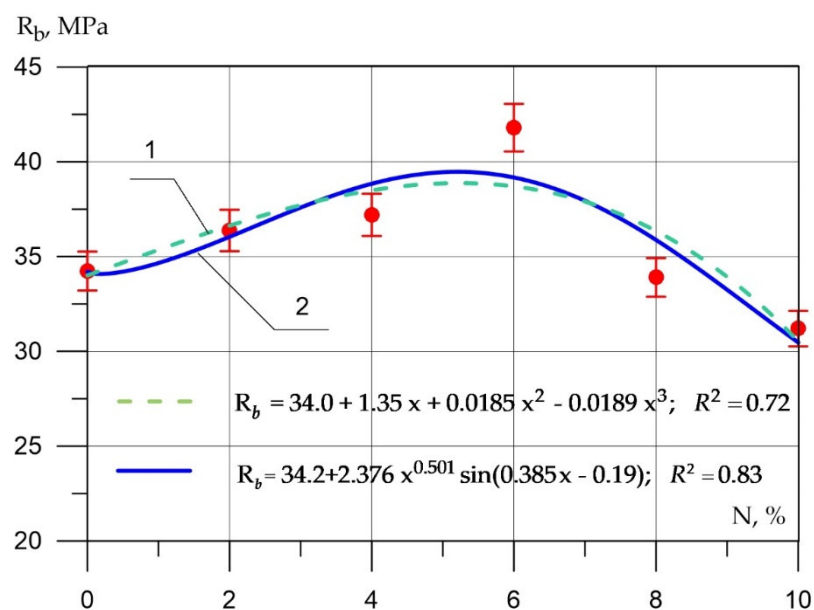


Figure 9. Results of experimental studies of the effect of dosage of rice straw biochar on axial compressive strength: 1—polynomial of the 3rd degree; 2—function (1).

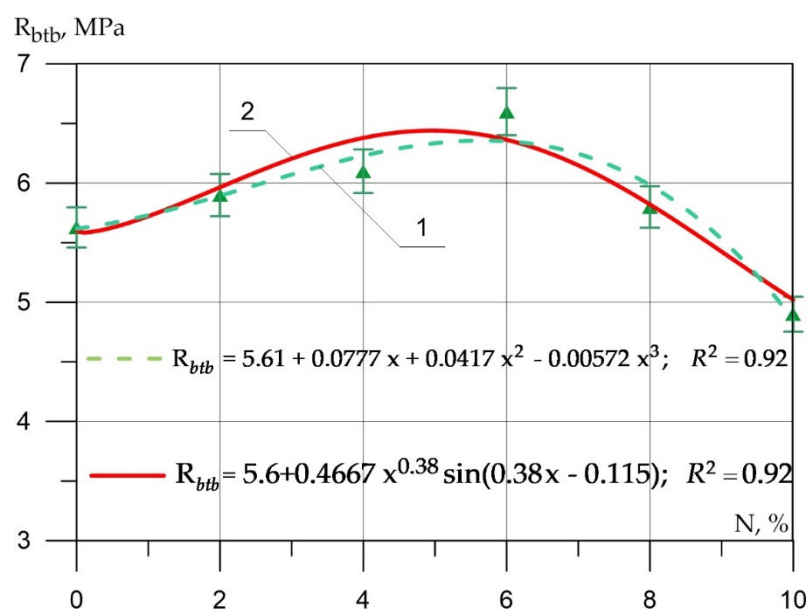


Figure 10. Results of experimental studies of the effect of dosage of rice straw biochar on flexural tensile strength: 1—polynomial of the 3rd degree; 2—function (1).

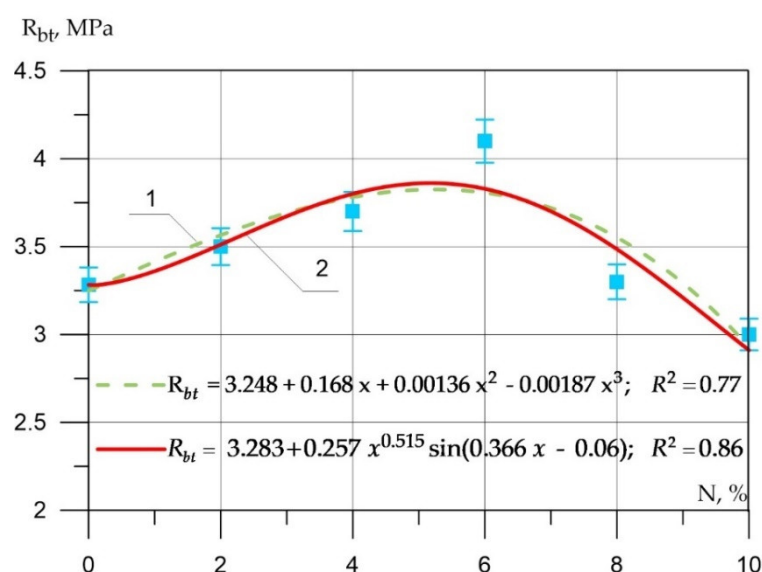


Figure 11. Results of experimental studies of the effect of dosage of rice straw biochar on axial tensile strength: 1—polynomial of the 3rd degree; 2—function (1).

Figure 8 shows the dependence of the cubic strength on the dosage of biochar N , %. For comparison, an approximation by a polynomial of degree 3 is given. It can be seen that function 1 better corresponds to the physical meaning of the processes that occur when the additive is introduced, and the coefficient of determination $R^2 = 0.90$ is higher than that of the polynomial.

A similar trend is observed for other strength characteristics presented in Figures 9–11.

Thus, the dependence of the strength characteristics on the dosage of rice straw biochar can be expressed by the formulas:

$$R_{b.cub} = 46.9 + 2.739 x^{0.5631} \sin(0.40697 x - 0.2626); \quad R^2 = 0.90 \quad (2)$$

$$R_b = 34.2 + 2.376 x^{0.501} \sin(0.385 x - 0.19); \quad R^2 = 0.83 \quad (3)$$

$$R_{btb} = 5.6 + 0.4667 x^{0.38} \sin(0.38 x - 0.115); \quad R^2 = 0.92 \quad (4)$$

$$R_{bt} = 3.283 + 0.257 x^{0.515} \sin(0.366 x - 0.06); \quad R^2 = 0.86 \quad (5)$$

Changes in the strength and deformation characteristics of test samples of heavy concrete, depending on the content of the rice straw biochar additive, are shown in Table 4 and are expressed as a percentage compared to the control composition (without additive).

Table 4. Changes in the strength and deformation characteristics of test samples of heavy concrete depending on the content of rice straw biochar additive (Δ).

Characteristics of Concrete	Change in % (Δ) with the Content of Rice Straw Biochar Additive, wt %					
	0	2	4	6	8	10
$R_{b.cub}$, MPa	0	+3	+10	+19	−2	−11
R_b , MPa	0	+6	+9	+22	−1	−9
R_{btb} , MPa	0	+5	+8	+17	+3	−13
R_{bt} , MPa	0	+7	+13	+25	+1	−9
ε_{bR} , mm/m $\times 10^{-3}$	0	−1	−5	−12	+2	+8
ε_{btR} , mm/m $\times 10^{-4}$	0	−3	−10	−24	−4	+8
$E_b = E_{bt}$, GPa	0	+4	+6	+14	−2	−6

The graphical dependencies and data on changes in the characteristics of concrete allow finding that the most effective dosage is the addition of rice straw biochar in an amount of 6% by weight of cement. This amount of additive allows for achieving maximum strength characteristics. Thus, the cubic compressive strength value was 55.7 MPa, the axial compressive strength was 41.8 MPa, the tensile strength in bending was 6.6 MPa, and the axial tensile strength was 4.1 MPa. It should be noted that the inclusion of biochar additives of 2% and 4% also contributes to the growth of strength characteristics. However, with the addition of biochar in an amount of 8%, an inverse relationship is observed, the values of the strength characteristics decreased and almost equaled the values of the strength characteristics of the control composition, and with the inclusion of an additive of 10%, and even more intense drop in strength characteristics was observed.

Additionally, according to the test results, diagrams of compression “ $\varepsilon_b - \sigma_b$ ” and tension “ $\varepsilon_{bt} - \sigma_{bt}$ ” were constructed. Graphic dependences of “stress-strain” are presented in Figures 12 and 13.

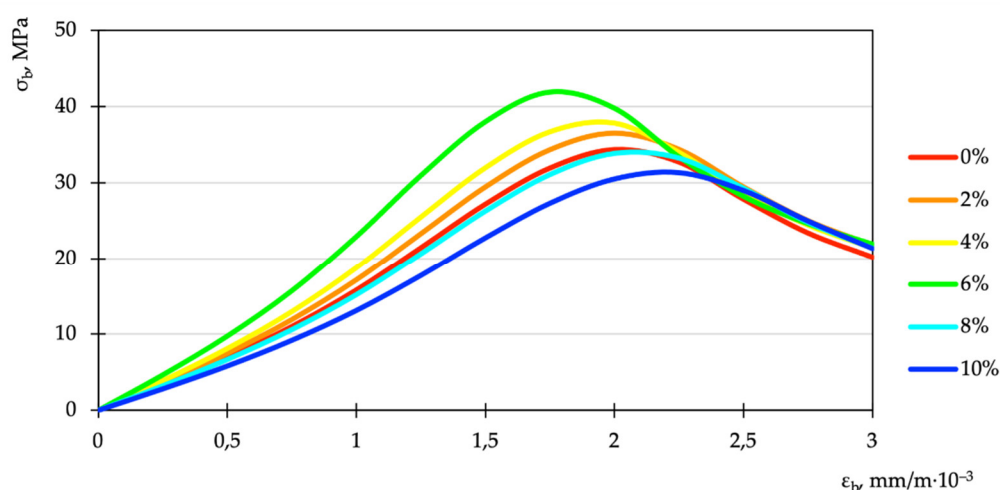


Figure 12. Stress-strain diagram in compression.

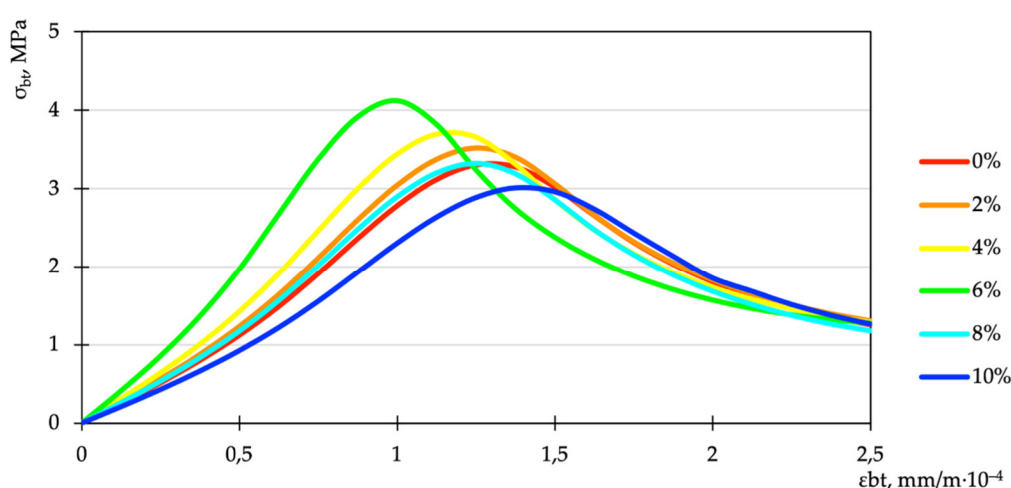


Figure 13. Tensile stress-strain diagram.

Based on the results of the analysis of the obtained deformation diagrams of concretes modified with the addition of rice straw biochar, the following conclusions can be drawn.

It has been established that the use of biochar additives affects the deformation diagrams of the resulting concrete as follows: the peak of the diagrams of concretes with the content of biochar additives in the amount of 2%, 4%, and 6% of the mass of cement shifts up and to the left relative to the diagrams of the control concrete sample, and the peak of the diagrams of concretes with the content of additives biochar in the amount of 8% and 10% is shifted up and to the right relative to the diagram of the control sample of concrete.

4. Discussion

In order to fully evaluate the contribution of the study to science and practice, one should compare the work performed with the work previously carried out by other authors [1–11,14–21,23–25,33–38]. Let us compare studies in terms of different approaches: methodology, technology, research, analysis, and practical applicability.

From the point of view of methodology, our study, for the first time, applied an integrated approach based on a detailed study of the characteristics of the product of processing agricultural waste—straw after its processing. Thus, we are primarily interested in a detailed analysis of the raw materials used, and then we identify the relationship between the final characteristics of the resulting concrete conglomerate nanomodified with processed rice straw biochar. Thus, we track each cycle of the study and fix the result at each stage step by step.

From the point of view of technology, the article has a difference in that it describes the methods of processing waste products and their disposal, prescription, and technological factors that affect the process of manufacturing a concrete conglomerate with nanomodification, and, thus, this technological approach is different from those previously carried out [1–11,14–21,23–25,33–38].

From the research point of view, we used various methods:

- Comparison of the results of the improved concrete with the results of the base sample;
- Mechanical and physical testing of samples in a number of experiments;
- Numerical processing and prediction of results due to the performed mathematical calculations and the determination of mathematical dependence;
- Microscopic analysis of the structure of raw materials for a detailed presentation and obtaining new knowledge and development of existing ideas about the raw materials used, which is the initial component for improved concretes.

Finally, all the necessary dependencies on the initial components are analytically fulfilled. The chemical, physical and mathematical aspects of the study were evaluated. Thus, the article is, at the same time, a scientific study aimed at obtaining new knowledge and developing existing ideas about concretes obtained from agricultural waste. At the same time, it has practical significance in view of the fact that it allows solving a significant problem not only of the construction complex, as the final consumer of our scientific and practical result, but also of agriculture, which, of course, can be an interested party and supplier of raw materials, which at present is in excess.

In terms of the result obtained, compared to the results obtained by other authors, an improvement in the increase in strength characteristics and other quantitative indicators of the obtained nanomodified concrete was achieved. Thus, the authors of works [5,16,19] obtained increases in strength characteristics at a 28-day age of concrete from 11% to 22% by modifying the composition with the addition of rice husk ash. Our technology and prescription recommendations have made it possible to increase the strength characteristics of concrete at 28 days of age from 17% to 25%. The “stress-strain” diagrams, built by us based on the results of the composition obtained by us, made it possible to identify an improvement in the deformation characteristics. Thus, the recipe-technological methods we used yielded an improved effect compared to the works performed earlier by other authors [5,16,19].

Thus, the article is not only of an applied technological nature but is also aimed at obtaining economic efficiency, the calculation of which is our next task, and the prospects

for the study can be defined as the direction of further work within the framework of scaling from technological to ecological and economic direction.

5. Conclusions

As a result of the study, we obtained several scientific and practical results.

- (1) A method for the disposal of agricultural waste has been proposed, and technology has been developed for use in concretes nanomodified with processed rice straw biochar.
- (2) The main parameters of the raw materials used are determined, and dependencies are established as a result of experiments, which are the development of existing theories and new knowledge for the agricultural and construction branches of science.
- (3) In the course of the research work, a sample of rice straw biochar modified by the electromagnetic method was obtained.
- (4) It has been established that the most effective dosage is the addition of rice straw biochar in the amount of 6% by weight of cement.
- (5) In a quantitative aspect, the improvement in the properties of concrete is expressed in the increase in its physical and mechanical characteristics and changes in deformability according to the results of the analysis of the stress-strain diagrams performed by us. The increase in characteristics was: for cubic compressive strength—19%, for prismatic compressive strength—22%, for axial tensile strength—25%, for tensile strength in bending—17%, for the elastic modulus—14%. The deformation characteristics decreased for deformation under axial compression—12%, for deformation under axial tension—24%.
- (6) According to our preliminary estimates, introducing a finely dispersed additive of rice straw biochar modified by the electromagnetic method leads to a decrease in cement consumption by up to 10%.
- (7) The results obtained demonstrated suitable compatibility of experimental data and the possibility of testing the technology in production conditions. The ecological and economic effects of the proposed technology and the manufactured material are noted.
- (8) At the microscopic level, a study of the used raw materials, which is obtained as a result of processing, was carried out, and its parameters are at the same time a new material and a springboard for further research, as well as the empirical and scientific data already obtained, are recommended for further research and practical application.

Author Contributions: Conceptualization, S.A.S., E.M.S. and A.N.B.; methodology, S.A.S., E.M.S. and A.S.S.; software, S.A.S., E.M.S., A.N.B. and N.B.; validation, N.B., S.A.S., E.M.S. and A.N.B.; formal analysis, A.S.S., S.A.S. and E.M.S.; investigation, L.R.M., S.A.S., E.M.S., A.N.B. and N.B.; resources, B.M.; data curation, S.A.S., E.M.S. and A.S.S.; writing—original draft preparation, S.A.S., E.M.S. and A.N.B.; writing—review and editing, S.A.S., E.M.S. and A.N.B.; visualization, S.A.S., E.M.S., A.N.B. and N.B.; supervision, L.R.M. and B.M.; project administration, L.R.M. and B.M.; funding acquisition, A.N.B. and B.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The study did not report any data.

Acknowledgments: The authors would like to acknowledge the administration of Don State Technical University for their resources and financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ductal-Ultra High Performance Concrete-a Revolutionary New Material for New Solutions. Imagine If It Were Made Out of Ductal, 38p. Available online: <http://www.apegm.mb.ca/pdf/PDPapers/ductal.pdf> (accessed on 26 May 2022).

2. Tang, L.V.; Bulgakov, B.; Aleksandrova, O.; Larsen, O.; Pham, A.N. Effect of rice husk ash and fly ash on the compressive strength of high performance concrete. *E3S Web Conf.* **2018**, *33*, 02030. <https://doi.org/10.1051/e3sconf/20183302030>.
3. Schmidt, M.; Fehling, E.; Geisenhanslüke, C. Ultra High Performance Concrete (UHPC). In Proceedings of the International Symposium on Ultra High Performance Concrete, Kassel, Germany, 13–15 September 2004; 884p. Available online: <https://www.uni-kassel.de/upress/online/frei/978-3-89958-086-0.volltext.frei> (accessed on 26 May 2022).
4. Wang, A.; Zhang, C.; Sun, W. Fly ash effects II. The active effect of fly ash. *Cem. Concr. Res.* **2004**, *34*, 2057–2060. <https://doi.org/10.1016/j.cemconres.2003.03.001>.
5. Bui, D.D.; Hu, J.; Stroeve, P. Particle size effect on the strength of rice husk ash blended gap-graded Portland cement concrete. *Cem. Concr. Compos.* **2005**, *27*, 357–366. <https://doi.org/10.1016/j.cemconcomp.2004.05.002>.
6. Stelmakh, S.A.; Shcherban, E.M.; Beskopylny, A.; Mailyan, L.R.; Meskhi, B.; Varavka, V. Quantitative and Qualitative Aspects of Composite Action of Concrete and Dispersion-Reinforcing Fiber. *Polymers* **2022**, *14*, 682. <https://doi.org/10.3390/polym14040682>.
7. Scrivener, K.L.; Vanderley, M.J.; Gartner, E.M. Eco-efficient cements: Potential economically viable solutions for a low-CO₂ cement-based materials industry. *Cem. Concr. Res.* **2018**, *114*, 2–26. <https://doi.org/10.1016/j.cemconres.2018.03.015>.
8. Klemm, W.; Berger, R. Accelerated curing of cementitious systems by carbon dioxide: Part I. Portland cement. *Cem. Concr. Res.* **1972**, *2*, 567–576. <https://doi.org/10.1016/0008-884690111-1>.
9. McDonald, L.; Glasser, F.P.; Imbabi, M.S. A New, Carbon-Negative Precipitated Calcium Carbonate Admixture (PCC-A) for Low Carbon Portland Cements. *Materials* **2019**, *12*, 554. <https://doi.org/10.3390/ma12040554>.
10. Goodman, B.A. Utilization of waste straw and husks from rice production: A review. *J. Bioresour. Bioprod.* **2020**, *5*, 143–162. <https://doi.org/10.1016/j.jobab.2020.07.001>.
11. Khan, M.N.N.; Jamil, M.; Karim, M.; Zain, M.; Kaish, A.B.M.A. Utilization of rice husk ash for sustainable construction: A review. *Res. J. Appl. Sci. Eng. Technol.* **2015**, *9*, 1119–1127. <http://dx.doi.org/10.19026/rjaset.9.2606>.
12. Beskopylny, A.; Stel'makh, S.A.; Shcherban, E.M.; Mailyan, L.R.; Meskhi, B. Nano modifying additive micro silica influence on integral and differential characteristics of vibrocentrifuged concrete. *J. Build. Eng.* **2022**, *51*, 104235. <https://doi.org/10.1016/j.jobe.2022.104235>.
13. Liu, H.; Li, Q.; Quan, H.; Xu, X.; Wang, Q.; Ni, S. Assessment on the Properties of Biomass-Aggregate Geopolymer Concrete. *Appl. Sci.* **2022**, *12*, 3561. <https://doi.org/10.3390/app12073561>.
14. Singh Aulakh, D.; Singh, J.; Kumar, S. The effect of utilizing rice husk ash on some properties of concrete—a review. *Curr. World Environ.* **2018**, *13*, 224–231. <http://dx.doi.org/10.12944/CWE.13.2.07>.
15. Hidalgo, S.; Soriano, L.; Monzó, J.; Payá, J.; Font, A.; Borrachero, M.V. Evaluation of Rice Straw Ash as a Pozzolanic Addition in Cementitious Mixtures. *Appl. Sci.* **2021**, *11*, 773. <https://doi.org/10.3390/app11020773>.
16. Ramezaniapour, A.A.; Mahdikhani, M.; Ahmadibeni, G. The effect of rice husk ash on mechanical properties and durability of sustainable concretes. *Int. J. Civ. Eng.* **2009**, *7*, 83–91.
17. Nair, D.G.; Fraaij, A.; Klaassen, A.A.K.; Kentgens, A.P.M. A structural investigation relating to the pozzolanic activity of rice husk ashes. *Cem. Concr. Res.* **2008**, *38*, 861–869. <https://doi.org/10.1016/j.cemconres.2007.10.004>.
18. Rukzon, S.; Chindaprasit, P.; Mahachai, R. Effect of grinding on chemical and physical properties of rice husk ash. *Int. J. Miner. Metall. Mater.* **2009**, *16*, 242–247. <https://doi.org/10.1016/S1674-479960041-8>.
19. Zareei, S.A.; Ameri, F.; Dorostkar, F.; Ahmadi, M. Rice husk ash as a partial replacement of cement in high strength concrete containing micro silica: Evaluating durability and mechanical properties. *Case Stud. Constr. Mater.* **2017**, *7*, 73–81. <https://doi.org/10.1016/j.cscm.2017.05.001>.
20. Habeeb, G.A.; Mahmud, H.B. Study on properties of rice husk ash and its use as cement replacement material. *Mat. Res.* **2010**, *13*, 185–190. <https://doi.org/10.1590/S1516-14392010000200011>.
21. Mubarik, S.; Qureshi, N.; Sattar, Z.; Shaheen, A.; Kalsoom, A.; Imran, M.; Hanif, F. Synthetic Approach to Rice Waste-Derived Carbon-Based Nanomaterials and Their Applications. *Nanomanufacturing* **2021**, *1*, 109–159. <https://doi.org/10.3390/nanomanufacturing1030010>.
22. Beskopylny, A.N.; Stel'makh, S.A.; Shcherban, E.M.; Mailyan, L.R.; Meskhi, B.; El'shaeva, D.; Varavka, V. Developing Environmentally Sustainable and Cost-Effective Geopolymer Concrete with Improved Characteristics. *Sustainability* **2021**, *13*, 13607. <https://doi.org/10.3390/su132413607>.
23. Hung, N.X.; Lam, T.V.; Bulgakov, B.I.; Aleksandrova, O.V.; Larsen, O.A.; Ky, H.H.; Melnikova, A.I. Effect of Rice Husk Ash on the Properties of Hydrotechnical Concrete. *Vestn. MGSU* **2018**, *13*, 768–777. <https://doi.org/10.22227/1997-0935.2018.6.768-777>.
24. Korobochkin, V.V.; Nguyen, M.H.; Usoltseva, N.V.; Nguyen, V.T. Production of activated carbon by pyrolysis of rice husk of Vietnam. *Bull. Tomsk Polytech. Univ. Geo Assets Eng.* **2017**, *328*, 6–15. Available online: <http://izvestiya.tpu.ru/archive/article/view/1877> (accessed on 13 December 2021).
25. Gorbunov, G.I.; Rasulov, O.R. Using Rice Straw to Manufacture Ceramic Bricks. *Vestn. MGSU* **2014**, *11*, 128–136. <https://doi.org/10.22227/1997-0935.2014.11.128-136>.
26. Lee, E.; Ko, J.; Yoo, J.; Park, S.; Nam, J. Effect of Dune Sand on Drying Shrinkage Cracking of Fly Ash Concrete. *Appl. Sci.* **2022**, *12*, 3128. <https://doi.org/10.3390/app12063128>.
27. Maljaee, H.; Madadi, R.; Paiva, H.; Tarelho, L.; Ferreira, V.M. Incorporation of biochar in cementitious materials: A roadmap of biochar selection. *Constr. Build. Mater.* **2021**, *283*, 122757. <https://doi.org/10.1016/j.conbuildmat.2021.122757>.

28. Sirico, A.; Bernardi, P.; Belletti, B.; Malcevski, A.; Dalcanale, E.; Domenichelli, I.; Fornoni, P.; Moretti, E. Mechanical characterization of cement-based materials containing biochar from gasification. *Constr. Build. Mater.* **2020**, *246*, 118490. <https://doi.org/10.1016/j.conbuildmat.2020.118490>.
29. GOST 7657-84 Charcoal. Specifications. Available online: <https://docs.cntd.ru/document/1200017215> (accessed on 13 December 2021).
30. GOST 24260-80 Wood Raw Material for Pyrolysis and Charring. Specifications. Available online: <https://docs.cntd.ru/document/1200014998> (accessed on 13 December 2021).
31. Yan, T.; Xue, J.; Zhou, Z.; Wu, Y. The Trends in Research on the Effects of Biochar on Soil. *Sustainability* **2020**, *12*, 7810. <https://doi.org/10.3390/su12187810>.
32. VOW-Valorization of Organic Waste. Available online: <https://www.ngi.no/eng/Projects/VOW-Valorization-of-Organic-Waste> (accessed on 14 February 2022).
33. Koushkbaghi, M.; Kazemi, M.J.; Mosavi, H.; Mohseni, E. Acid resistance and durability properties of steel fiber-reinforced concrete incorporating rice husk ash and recycled aggregate. *Constr. Build. Mater.* **2019**, *202*, 266–275. <https://doi.org/10.1016/j.conbuildmat.2018.12.224>.
34. Alyousef, R.; Ali, B.; Mohammed, A.; Kurda, R.; Alabduljabbar, H.; Riaz, S. Evaluation of Mechanical and Permeability Characteristics of Microfiber-Reinforced Recycled Aggregate Concrete with Different Potential Waste Mineral Admixtures. *Materials* **2021**, *14*, 5933. <https://doi.org/10.3390/ma14205933>.
35. Wani, I.; Kumar, H.; Rangappa, S.M.; Peng, L.; Siengchin, S.; Kushvaha, V. Multiple regression model for predicting cracks in soil amended with pig manure biochar and wood biochar. *J. Hazard. Toxic Radioact. Waste* **2021**, *25*, 04020007 [https://doi.org/10.1061/\(ASCE\)HZ.2153-5515.0000561](https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000561).
36. Rangappa, S.M.; Siengchin, S.; Parameswaranpillai, J.; Jawaid, M.; Ozbakkaloglu, T. Lignocellulosic fiber reinforced composites: Progress, performance, properties, applications, and future perspectives. *Polym. Compos.* **2022**, *43*, 645. <https://doi.org/10.1002/pc.26413>.
37. Nagarajan, K.J.; Ramanujam, N.R.; Sanjay, M.R.; Siengchin, S.; Rajan, B.S.; Basha, K.S.; Madhu, P.; Raghav, G.R. A comprehensive review on cellulose nanocrystals and cellulose nanofibers: Pretreatment, preparation, and characterization. *Polym. Compos.* **2021**, *42*, 1588–1630. <https://doi.org/10.1002/pc.25929>.
38. Jagadeesh, P.; Puttegowda, M.; Mavinkere Rangappa, S.; Siengchin, S. Influence of nanofillers on biodegradable composites: A comprehensive review. *Polym. Compos.* **2021**, *42*, 5691. <https://doi.org/10.1002/pc.26291>.
39. Tolmacheva, V.V.; Apyari, V.V.; Kochuk, E.V.; Dmitrienko, S.G. Magnetic sorbents based on iron oxide nanoparticles for the isolation and concentration of organic compounds. *Zhurnal Anal. Khimii* **2016**, *71*, 339–356. <https://doi.org/10.7868/S0044450216040071>.
40. Golovko, M.I.; Goncharenko, Y.V.; Gorobets, V.N.; Zotov, S.M. Installation for the regeneration of sorbents in an electromagnetic field. *Technol. Des. Electron. Equip.* **2005**, *5*, 49–51. Available online: <http://dspace.nbuv.gov.ua/bitstream/handle/123456789/53632/13-Golovko.pdf?sequence=1> (accessed on 13 December 2021).
41. GOST 10180 Concretes. Methods for Strength Determination Using Reference Specimens. Available online: <https://docs.cntd.ru/document/1200100908> (accessed on 13 December 2021).
42. GOST 24452 Concretes. Methods of Prismatic, Compressive Strength, Modulus of Elasticity and Poisson's Ratio Determination. Available online: <https://docs.cntd.ru/document/9056198> (accessed on 13 December 2021).
43. GOST 18105 Concretes. Rules for Control and Assessment of Strength. Available online: <https://docs.cntd.ru/document/1200164028> (accessed on 14 December 2021).
44. Stel'makh, S.A.; Shcherban, E.M.; Beskopylny, A.N.; Mailyan, L.R.; Meskhi, B.; Butko, D.; Smolyanichenko, A.S. Influence of Composition and Technological Factors on Variatropic Efficiency and Constructive Quality Coefficients of Lightweight Vibro-Centrifuged Concrete with Alkalized Mixing Water. *Appl. Sci.* **2021**, *11*, 9293. <https://doi.org/10.3390/app11199293>.
45. Shcherban, E.M.; Stel'makh, S.A.; Beskopylny, A.; Mailyan, L.R.; Meskhi, B.; Varavka, V. Nanomodification of Lightweight Fiber Reinforced Concrete with Micro Silica and Its Influence on the Constructive Quality Coefficient. *Materials* **2021**, *14*, 7347. <https://doi.org/10.3390/ma14237347>.
46. Shcherban, E.M.; Stel'makh, S.A.; Beskopylny, A.; Mailyan, L.R.; Meskhi, B. Influence of Mechanochemical Activation of Concrete Components on the Properties of Vibro-Centrifuged Heavy Concrete. *Appl. Sci.* **2021**, *11*, 10647. <https://doi.org/10.3390/app112210647>.
47. Stel'makh, S.A.; Shcherban, E.M.; Beskopylny, A.; Mailyan, L.R.; Meskhi, B.; Dotsenko, N. Enchainment of the Coefficient of Structural Quality of Elements in Compression and Bending by Combined Reinforcement of Concrete with Polymer Composite Bars and Dispersed Fiber. *Polymers* **2021**, *13*, 4347. <https://doi.org/10.3390/polym13244347>.