INTERNATIONAL SYMPOSIUM

Print: ISSN 2344 - 4118
CD-ROM: ISSN 2344 - 4126
Online: ISSN 2537 – 3773
ISSN-L 2344 – 4118

ISB-INMA TEH

AGRICULTURAL AND MECHANICAL ENGINEERING

Bucharest
6-8 October 2022

ISB-INMA TEH

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Print: **ISSN 2344 - 4118**
CD-ROM: **ISSN 2344 - 4126**
Online: **ISSN 2537 - 3773**
ISSN-L 2344 – 4118

Indexed in CAB DIRECT, http://www.cabdirect.org/ , **Index Copernicus**

Edited: **INMA Bucharest & SIMAR**

APPLICATION OF BIOCHAR OF DIFFERENT GENESIS: APPLIED ASPECTS OF ACTIVATION
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ЗАСТОСУВАННЯ БІОЧАРУ РІЗНОГО ПОХОДЖЕННЯ: ПРИКЛАДНІ АСПЕКТИ АКТИВАЦІЇ

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Keywords: *biochar, activation, biogas, biofertilizer, ultrasonic pretreatment*

ABSTRACT
The paper considers various biochar activation processes in bioprocesses, particularly in anaerobic digestion, to intensify the production of biogas and biofertilizer. Based on the literature research study, the applied aspects of biochar activation processes in the agricultural and bioenergy sectors were analyzed, with small-scale laboratory experiments to verify theoretical hypotheses. Ultrasonic pretreatment was performed with a power of 200 W and a frequency of 30 kHz. The biochar was also subjected to microscopy. After ultrasound treatment, changes in the structure of biochars of different genesis were detected, which is also consistent with changes in the ORP values of activated biochars. A comparative thermogravimetric analysis of biochar samples was carried out.

ТЕЗИ
У статті розглядаються різні варіанти активації біовугілля у біопроцесах, зокрема в анаеробному зброджуванні, для інтенсифікації виробництва біогазу та біодобрив. На основі вивчення літератури було проаналізовано прикладні аспекти процесів активації біовугілля у сільськогосподарському та біоенергетичному секторах, а також проведено дрібномасштабні лабораторні експерименти для перевірки теоретичних гіпотез. Ультразвукова попередня обробка проводилася при потужності 200 Вт та частоті 30 кГц. Біочар також піддавався мікроскопії. Після ультразвукової обробки були виявлені зміни в структурі біочарів різного генезису, що також узгоджується зі зміною значень ОВП активованих біочарів. Порівняльний термогравіметричний аналіз зразків биочара було проведено.

INTRODUCTION
Today, the use of biochar in various spheres of human economic activity has become increasingly widespread. Biochar is a solid material containing carbon with a large amount of hard-mineralized aromatic structures, obtained by carbonization of renewable organic biomass at high temperatures and without oxygen access (pyrolysis) (*Edinburgh Research Explorer Biochar Quality Mandate (BQM) Version 1.0*, n.d.).

Periodically, the term "biochar" is associated with the term "charcoal," which is obtained in the process of producing lumpy charcoal, which does not correspond to the definition of biochar. Biochar is also a plant-derived charcoal with a carbon content of 93-99% and the absence of harmful and toxic impurities. Due to its main properties - purity and absence of impurities, as well as high carbon saturation, biochar can be used in agriculture - both in animal husbandry and in the agricultural sector (*Kamarudin et al., 2022*) (*Kamarudin et al., 2022*).

Biochar as an additive in agriculture has the following advantages (*Biochar, the benefits of using natural soil fertilisers – Proposition, 2020*)**:**

- speeds up plant growth and development as the soil is constantly heated;
- removes residues from the soil of chemicals that were applied earlier (herbicides, pesticides, and other pesticides);

- promotes the functioning of microorganisms in the soil, which have a positive effect on crop yields;
- increases soil porosity, provides oxygen access to plant roots, and air circulation;
- improves the composition of infertile soils (alumina, sandy ,loam and sandy soils);
- neutralize soils with increased acidity;
- protects soil from some pests (nematodes, wireworm);
- prevents purulent processes;
- preserves and supports nutrients and necessary microelements in the soil, and eliminates the problem of their leaching.

It also serves as a raw material for the production of activated carbon, is used for drinking water and wastewater treatment, for the elimination of toxins and disinfection, and is used in segments of industry where there is a need for pure carbon. For example, in Germany, biochar is actively used in agriculture as ready-to-use mail mixed and as a soil substrate. It is also used as a food additive for cattle, birds and pets. Biochar is a high-value-added processed product with a very broad testing potential; its production solves the current problem of waste recycling, contributes to the introduction of "green technology" and the production of bioenergy (*Biochar And The Biomass Recycling Industry | BioCycle, 2011*).

Of particular importance in some biochemical processes is the high resistance to the chemical reaction and resistance to swelling of adsorbents. In this aspect, carbon adsorbents compare favorably with mineral- and polymer-basedĂ adsorbents, which opens up wide opportunities for their practical use. In this direction, we can also consider biochars, and there are electrochemical features of biochars, which are now actively investigated and can be applied in biogas technologies.

Regarding the activation of coals of different nature, a number of works (*Bisaria et al., 2022; Peter et al., 2019, 2020; Y. Wu et al., 2016*) studied the effect of the type of processing (mechanical, ultrasonic) on the degree of dispersion, density of carbon powders, and their morphology; samples of "carbon powders" with sieve properties obtained by different methods determined their structural characteristics (*Stavitskaya, 2009*).

Ultrasound treatment is a means of active influence on various structures of substances (*Moskalenko & Danilov, 2009*):

i. on the course of heat and mass exchange processes in substances;
ii. on the structure of solids and processes of their contact interaction.

The use of ultrasonic sound in technological processes of production and processing of materials and substances allows (*Kamarudin et al., 2022; L. Wu et al., 2022; Moskalenko & Danilov, 2009*):

i. reduce the cost of a process or product;
ii. obtain new products or improve the quality of existing ones;
iii. to intensify traditional technological processes or stimulate the implementation of new ones.

In this regard, the problem of identifying the nature of the specific effects of acoustic ultrasonic vibrations on the processes of deep processing of raw materials is relevant. The idea of the implementation of combined processes in obtaining active coals of different genesis, including biochar, has been developed in a number of studies (*Kizito et al., 2022; Kobayashi & Kuramochi, 2022; Liu et al., 2022; Zhang et al., 2022; Zhao et al., 2022*). The technology for obtaining charcoal by combined pyrolysis-vapor-gas activation using alternating electric current has been proposed. Ways of directed regulation of the porous structure parameters and adsorption properties of wood active carbons have been investigated. Processes of activation of coals at processing by a constant electrolytic field by a voltage in a diapason 1.5-30 V lead to the reception of hydrogen-activated charcoal. When used in aqueous solutions, this charcoal is negatively charged, sending hydrogen ions into the solution and attracting cations, which intensifies the purification process (*Belyaev, 2000*).

Rapid pyrolysis of biomass pretreated with mineral acid produces high-quality biofuels, but the biochar resulting from this process has not been characterized, and its effectiveness as an additive for aanaerobic digestion (AD) is unknown. This study reports the effect of the physicochemical properties of two different biochars on AD of urban sludge: one was produced by pyrolysis of raw corn cobs (BC-1) and the other was produced by pretreatment of the same corn cobs with sulfuric acid (BC-2). BC-1 had higher carbon content, alkalinity and specific surface area, but lower ash and sulfur content than BC-2. Both biochars contained volatile fatty acids and residual sugars that serve as substrates for anaerobic bacteria to improve biogas / methane production. When biochars were added to AD, their effect on biogas production showed opposite trends. In general, the results showed that the effect of biochar on AD depends on the properties of the biochar, and the choice of a suitable biochar is important to ensure higher biogas production and to maintain a stable process (*Zhou et al., 2020*).

A study (*Wambugu et al., 2019*) evaluated the effect of biochar addition on anaerobic digestion (AD) of food waste. Of the five biochar tested, Fe, Co, Ni, and Mn leached in very small amounts (<10 mg/kg), while treated wood waste and willow pyrochar leached large amounts of K (1,510 and 1,969 mg/kg), respectively. AD experiments were carried out in a 1:1 inoculum:substrate ratio, at 30°C and under stirring conditions. The results showed that the volume of biogas produced by treatment with hydrosugar from brewery residues and pyrosugar from treated wood was lower than that produced by a control that used only food waste. Food waste supplemented with 1.5 ml of micronutrients produced the highest amount of biogas, 588 ml/g COD (CH_4 content 48%). In addition, two identical upflow anaerobic sludge reactors (UASB), that is, the control reactor and the biochar supplemented reactor, operated at 30°C, with organic loading rates (OLR) ranging from 3.4 to 7.8 g COD/L per day. The average COD removal efficiency in the control reactor and the biochar-added reactor was 47% and 77% at OLRs of 6.9 to 7.8 g COD/L. per day, respectively. The results clearly show that the type of biochar and its trace element concentration play a key role in determining its effectiveness in improving the production of biogas from food waste (*Wambugu et al., 2019*).

Biochar can receive and give out electrons, as in microbial fuel cells, where biochar can be activated and used as an anode and cathode (*Patwardhan et al., 2022*). However, the electrical conductivity of biochar is not based on a continuous flow of electrons, as in copper wire; it is based on continuous electron hopping, which is important for the functioning of biochar as a microbial electron mediator or so-called electron boat, which facilitates even inter-species transfers. Because of the relatively large size of the biochar particles, the electron transfer capacity of the biochar carbon matrices can lead to the exchange of electrons over considerable distances, allowing greater access to alternative acceptors, such as those of minerals, for oxygen-free microbial respiration. We assume that it can also be used effectively in electrolysis processes of the substrate to intensify anaerobic digestion, which requires experimental studies.

Thus, the purpose of this work is to study the possible applied use of biochar in anaerobic digestion with an experimental study of the effect of ultrasonic treatment on the properties of biochar.

MATERIALS AND METHODS

Ultrasonic pretreatment was performed in a stainless steel tube section with a total working volume of 250 ml. Ultrasonic equipment, consisting of 3 transducers, with a power of 200 W and a frequency of 30 kHz was placed in the section.

Fig. 1 shows the laboratory experimental installation of ultrasonic treatment.

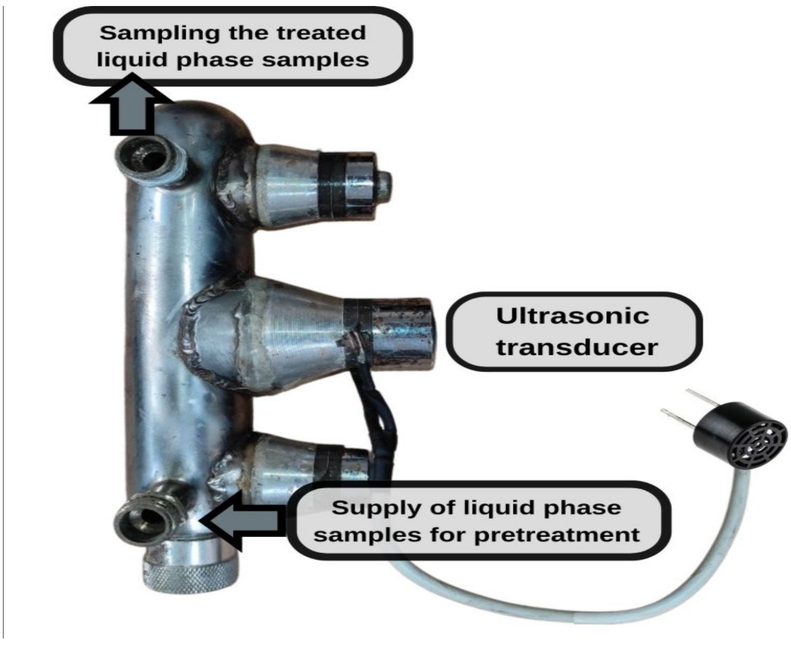


Fig. 1 - Laboratory device for ultrasonic treatment

The ultrasonic treatment unit works as follows: The treated liquid enters the treatment tank through special holes in which the solution is poured manually, which provides uniform distribution over the entire cross-sectional area of the chamber. Ultrasonic vibrations are formed in the process. The direction of propagation of the ultrasonic vibrations is perpendicular to the surfaces of the smooth transitions. Thus, the ultrasonic field with the intensity necessary and sufficient for the formation and maintenance of the developed cavitation mode is created in the entire space between the walls of the unit and the surface of the radiator in the internal volume of the tank.

Temperature mode - 35 ^{0}C. Processing time: 1 min. Light microcopying was used to identify changes in the structure of the samples using a biological XS-5520 microscope with a video camera.

A comparative thermogravimetric analysis of biochar samples made from wood residues and corn stalks was carried out to obtain information about their thermal stability using the derivatograph Q-1500D of the “F. Paulik-J. Paulik-L. Erdey” system. Differential mass loss and heating effects were recorded. The measurements results were processed with the software package supplied with the device. Samples of wood and bark biomass were dynamically analyzed at a heating rate of 10°C/min in the air atmosphere. The weight of the samples was 100 mg. Aluminum oxide was used as the reference substance.

RESULTS

Results of ultrasound treatment of biochars of different genesis

In the study, two types of biochar were taken: one produced from corn residues, the other by pyrolysis of wood residues from the furniture industry (Fig.2).

Fig. 2 – Biochars:
a - from plant residues (corn); b - from wood residues from the furniture industry.

Table 1 shows the pH and ORP values before and after ultrasonic treatment of biochars of different genesis.

Table 1

Changes in the parameters of the treated liquid phase with biochar

Composition	Volume of water	Sonication treatment	TDS	pH	ORP
2.5 g biochar (a)	250 ml	before treatment	363	10.5	-49
		after treatment	457	10.5	-20
2.5 g biochar (b)		before treatment	844	11.3	-50
		after treatment	746	11.22	-50

Microcopying of the biochars was also performed. It should be noted that the initial high porosity of biochar (b), compared to biochar (a) (Fig. 3).

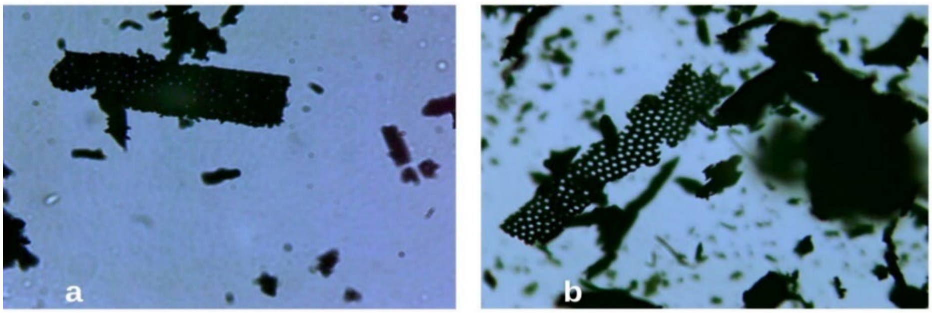


Fig. 3 - Biochars before treatment, microscopy, 40x magnification:
a - from plant residues (corn); b - from wood residues from the furniture industry.

After ultrasound treatment, more influence was revealed on biochar (a) during microscopy, which is also consistent with the change in its ORP values (it increased from -49 to -20 mV). The structure of biochar (a) became much more homogeneous with high fine fraction content, when drying preparations for microscopy of biochar (a) it sorbed water better compared to biochar (b) (Fig. 4 and 5).

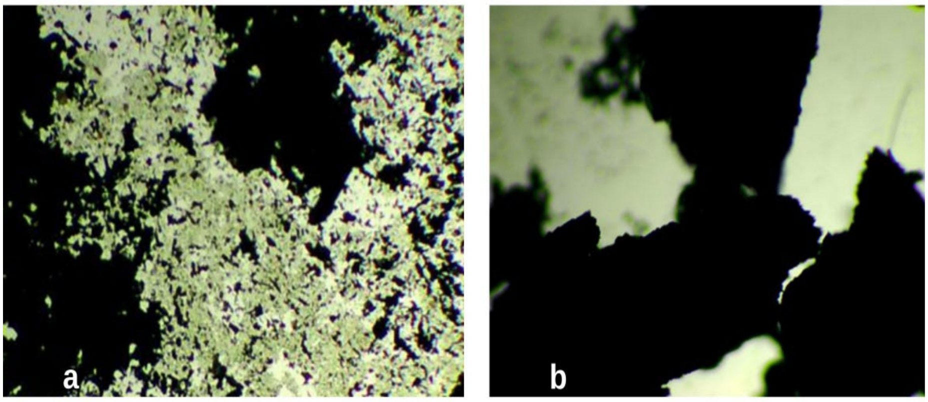


Fig. 4 - Biochars after treatment, microscopy, 4x magnification:
a - from plant residues (corn); b - from wood residues from the furniture industry.

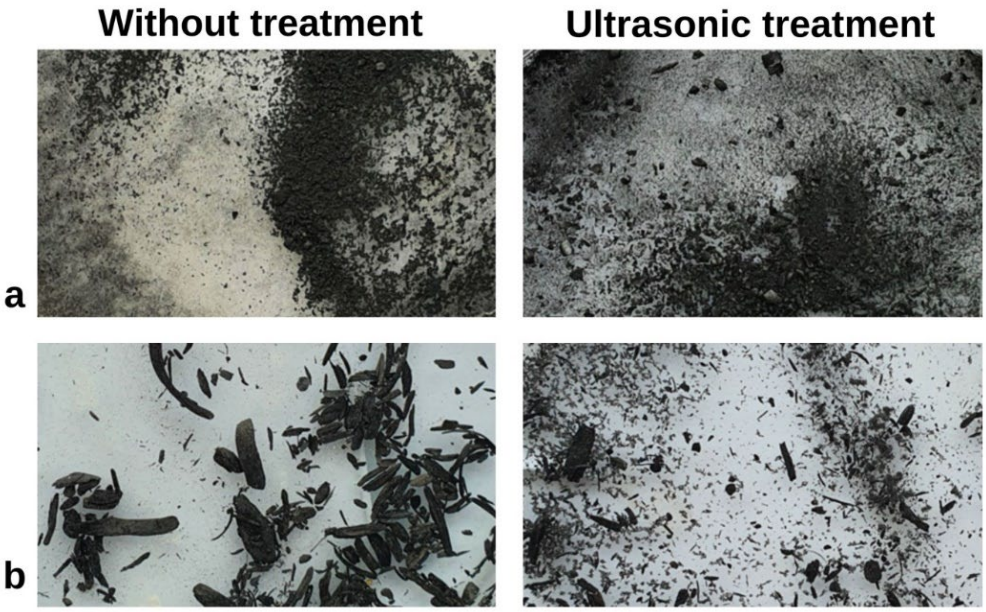
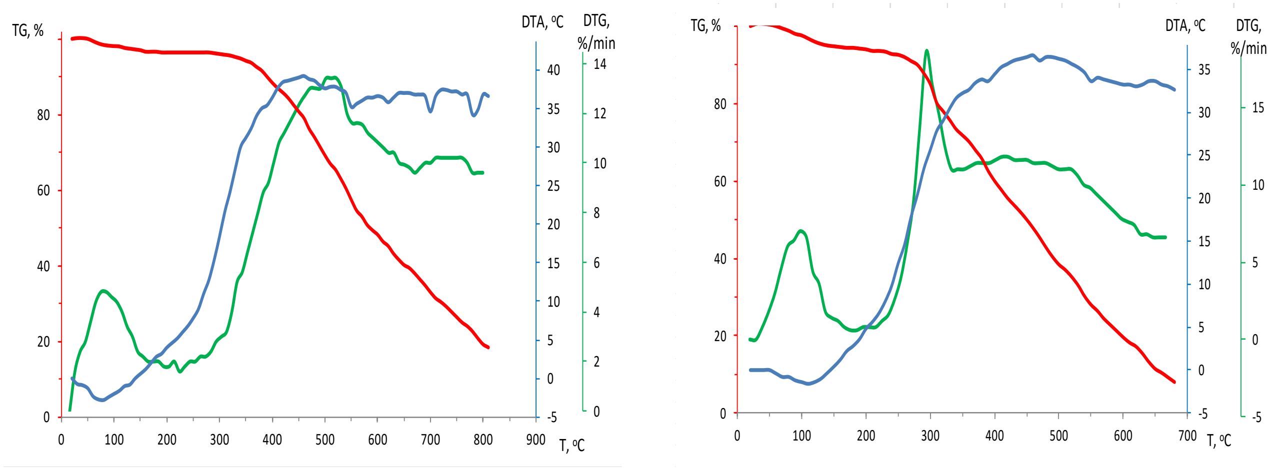


Fig. 5 - Comparison before and after ultrasonic treatment:
a - from plant residues (corn); b - from wood residues from the furniture industry.

The TG and DTG combustion curves were analyzed for thermal stability of the two types of biochar made from wood residues and corn stalk (Fig.6).



a b

Fig. 6 - TG, DTA and DTG of biochar produced from:
a - wood residues; b - corn biomass

According to the DTG curves the first thermal peaks that occurred within 75 - 100^{0}C. As visible in Fig. 6, the moisture of the biochars produced was retained after the preliminary pyrolysis procedure, which is consistent with the findings of Li and Chen (2018). . Thus, these types of biochar can be used as water sorbents to improve moisture retention in the soil. The thermal peaks at 200 - 400 ^{0}C are associated with the loss of hemicellulose and cellulose, whereas the peaks at 370 - 550^{0}C are associated with the thermal decomposition of lignin. The sharp peak fixed at 300 - 480^{0}C fixed for biochar from corn biomass can be explained as a result of the autocatalytic reaction of hemicellulosic, cellulosic, and lignocellulosic components (*Yang et al., 2007*). Thus, the pyrolysis process was a reason for the formation of more thermostable substances in the tested biochar samples.

Formalization of the direction of use of biochar together with digestate in soil bioremediation processes

Anaerobic digestion is an effective method for processing raw materials of organic origin. The passage of raw material and its composition is one of the key points of processing. Anaerobic digestion can be successful even with heavy metal contaminated raw materials provided that biochar is added as an additive. Accordingly, the study (*Wang et al. 2021*), although the environmental risk of heavy metals (HM) in digestate can potentially increase during anaerobic digestion of contaminated feedstock, states that biochar contributes to the passivation of heavy metals in the process.

Furthermore, HM passivation by (*Wang et al. 2021*) also obtained the result of increased biogas productivity in an example of contaminated pig manure. The methane yield increased up to 26% with the addition of additives up to 7% biochar (on a dry weight basis). Different groups of heavy metals were also found to passivate faster at different concentrations of biochar (5% and 7%).

Fig. 7 shows the main characteristics of biochar conditioning a successful combination with digestate for soil remediation applications. In the process of obtaining the target product of biofuel, digestate is formed, which is an important product for the restoration of soil quality. To maintain the normal functioning of the soil-biota system of soils contaminated with HMs and radionuclides, a comprehensive approach to cleaning and increasing productivity is necessary. Biochar and digestate independently of each other have properties to reduce the concentration of heavy metals in soil solution. A study (*van Poucke et al., 2020*) compares the potential of biochar in different raw materials and digestate applications to highlight the potential to immobilize metals in soil and aquatic systems, reducing phytotoxicity.

Biochar and products based on it as agents for the immobilization of toxic substances, including HM contained in the soil, can be an environmentally friendly solution for soil remediation.

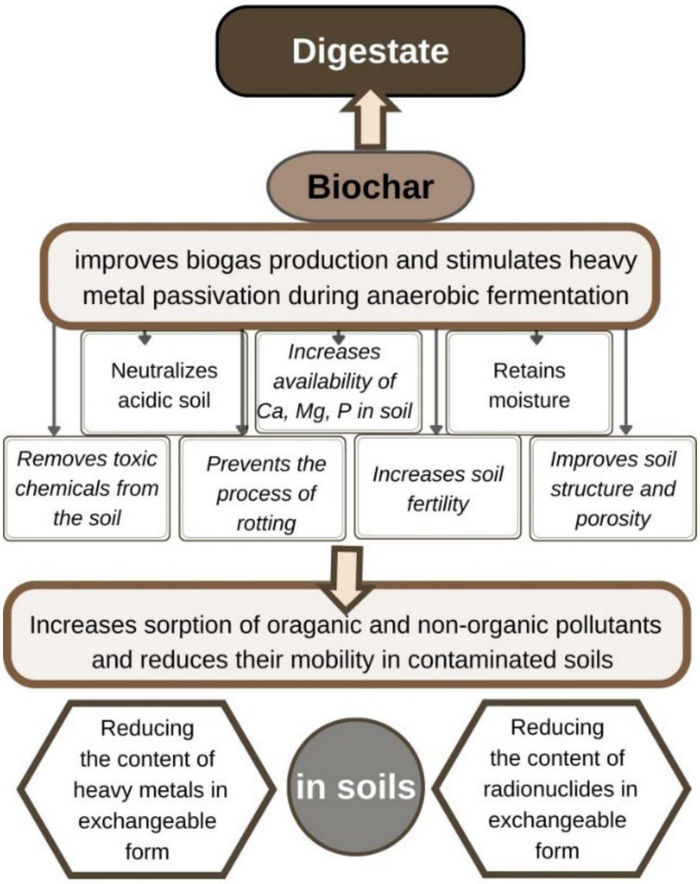


Fig. 7 - Impact of biochar on the soil structure

The use of biochar helps solve the problem of the bioavailability of heavy metals as a result of the direct application of its mixture to rigid digestate. (*Xue et al., 2021*) conducted an experiment using fruit biochar and porcine digestate to clean cadmium-contaminated greenhouse soil. The advantages of co-application were the ability to maintain a more stable pH and electrical conductivity and to effectively improve the properties of organic matter of soil with a reduction in the activity of a particular group of heavy metals. It was shown that the bioavailability of heavy metals and enzyme activity are related to the proportion of biochar-digestate mixing.

Research by *Anae et al. (2021*) also looked at the microbiological characteristics of the combination, where the study showed the promising potential of digestate as a source of nutrients and bacteria for soil bioremediation. In summary, biochar-digestate can be engineered by bioengineering to contain selected microbial consortiums that will incorporate a biochemical system that will facilitate remediation of contaminated soil beyond conventional methods. A related study Šimanský et al. (2022) demonstrates different effects of a biochar-based composite application, depending on soil texture, cation exchange capacity, organic carbon content, and stability of the humic substance.

The work found that for productive, fertile, and alkaline soils uncontaminated with HM, changes in macronutrient regime after the application of biochar-based composite are insignificant but can be influenced by soil texture. However, the application of such composites with fertilizers leads to changes in the physical and chemical properties of the soil and a variety of benefits in sandy and loamy soils. It was traced the dependence after the application of composites that the immobilization of heavy metals is caused by the higher content of organic carbon and fulvic acids in sandy soils,soils, while in loamy soil their elimination depended on the higher content of available phosphorus.

Based on these and previous studies, we have developed a scheme (Fig. 8) that positively influenced the use of biocomposite based on digestate and biochar in combination with phytoremediation.

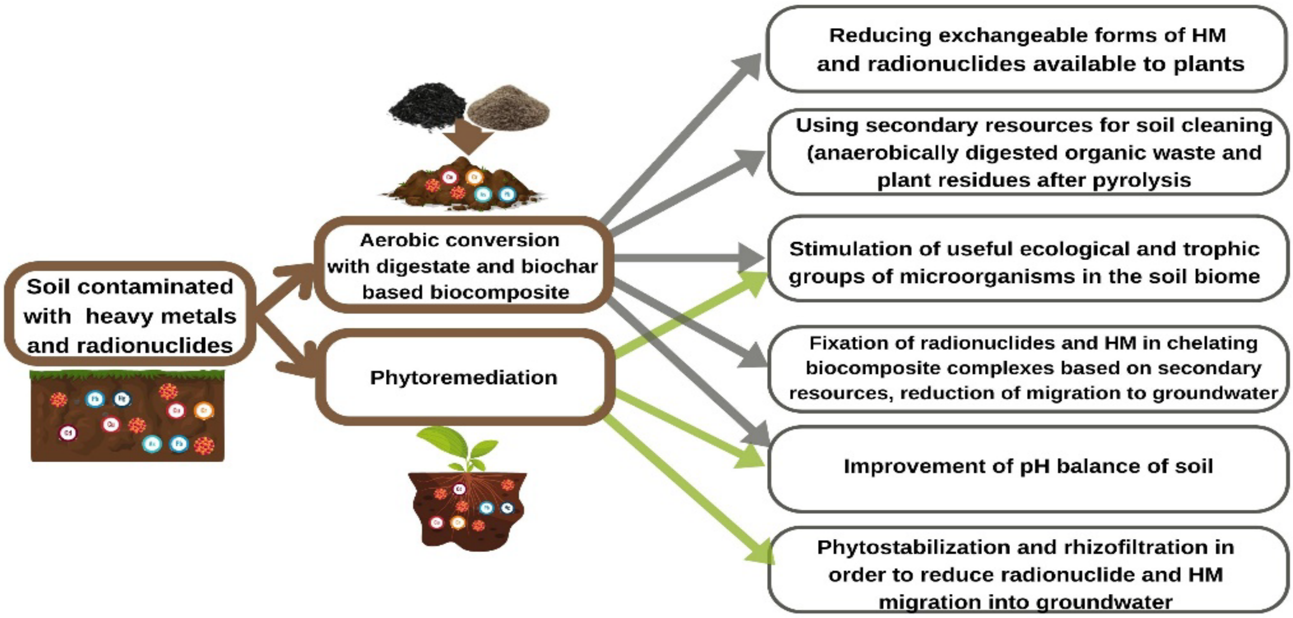


Fig. 8 - Impact of remediation methods for soils contaminated with heavy metals and radionuclides

Furthermore, digestate pyrolysis to produce biochar has been investigated in recent years (*Ayaz et al., 2022; Chen et al., 2019; N. Wang et al., 2022; Zuo et al., 2020*), as pyrolysis can stabilize the metals in biochar.

The potential applications of biochar derived from high moisture digestate could be as an adsorbent to remove contaminants, as a soil amendment to enhance plant growth, and as a catalyst to improve bioprocessing (*N. Wang et al., 2022*).

Although conventional technologies exist to address contaminated soils, the use of biochar-based biocomposite as an effective recoverable adsorbent for enhanced bioremediation is considered by many researchers to be a promising strategy to mitigate the effects of co-contamination of soils with HM and radionuclides.

CONCLUSIONS

Biochar is an effective adsorbent with a wide range of applications in terms of its physicochemical characteristics. The activation of biochar affects the morphological structure of the particles and leads to a certain change in the physicochemical parameters of the substance with the biochar compound. Furthermore, an opportunity to use biochar in biogas technology in various combinations is considered.

However, combinations of biochar and digestate as an effective soil improver for the remediation of soils contaminated with heavy metals and radionuclides are recommended to be the focus of further research. Biocomposites based on digestate and biochar have the advantage of cleaning and improving soil conditions and plant growth and can be found in different combinations.

ACKNOWLEDGEMENT

This research project was carried out as planned research projects of the Department of Ecology and Environmental Protection Technologies of Sumy State University, related to the topics “Assessment of the technogenic load of the region with changes in industrial infrastructure” according to the scientific and technical program of the Ministry of Education and Science of Ukraine (state registration No 0121U114478); Joint

Ukrainian-Czech R&D project “Bioenergy innovations in waste recycling and natural resource management”, 2021-2022.

We are thankful to the Czech government support provided by the Ministry of Foreign Affairs of the Czech Republic, which allowed this scientific cooperation to start within the project “AgriSciences Platform for Scientific Enhancement of HEIs in Ukraine.

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