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SUMMARY

„The use of natural carbon-bearing materials in useful products' technologies"

The doctoral dissertation entitled 'The use of natural carbon-bearing materials in useful products' technologies' focuses on the development of new humic preparations and the conversion of post-process residues into a biochar products. The use of obtained humic acids and biochars as substrates in the production of formulations of useful products for agricultural applications is proposed. The subject matter of this PhD thesis falls within the areas of chemical technology and engineering, environmental protection and agricultural chemistry.

The main objective of the research work was to develop methods for obtaining humic acids and biochars with parameters that allow their use in agricultural preparations. On the basis of the analysis of literature reports, patents and patent applications described in the literature part of this dissertation, in which the state of the art is presented, a selection of carbon-bearing raw materials was made. Considering the further possibilities of using the developed products, domestic natural raw materials, peat and brown coal, were selected for the research.

The literature part of the dissertation includes current information from scientific publications and patent documentation on humic substances, their classification, characteristics, properties and impact on soil and plant crops. Other applications of humic substances include studies relating to economic sectors, such as animal husbandry, cosmetics and therapeutics. Reports on the production and use of biochar from biomass in the perspective of post-extraction residue management are presented. The obtaining of humic substances by alkaline extraction methods was analyzed. Important aspects of the newly developed technologies are market research, demand for the manufactured products, their quality, availability of raw materials, etc. The literature review also focuses on scientific studies and technical solutions that meet environmental protection requirements, in line with the principles of Sustainable Development, Circular Economy and Resource-Efficient Economy.

In the experimental part, the aim and scope of the research were defined. Based on the literature part, publications and standards, the research methodology and analytical approach were selected and modified. Research and analytical methods, used in comparable studies, were included in the field of evaluation of isolated humic fractions and obtained biochars regarding their projected agricultural applications. To assess the useful properties of raw materials, humic acids or biochars, as well as possible products based on them, and to evaluate operations and technological processes, the following methods and analytical techniques were selected:

- determination of moisture content,
- determination of ash content,
- determination of content of humic acids gravimetrically based on the international standard ISO 19822:2018,
- determination of C, H, N, S, O content by elemental analysis,
- performance of Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR) spectroscopic spectra for determination of the structure of the substance,
- performance of Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FTIR) spectroscopic spectra for identification of main functional groups,
- determination of presence of functional groups by potentiometric titration with determination of surface negative charge and distribution functions of apparent surface dissociation constants.

The research was conducted on a laboratory scale. Given the environmental protection requirements, an important aspect of the dissertation was to develop a technology that considers the possibility of managing the post-extraction residues generated in the process. The technological process for obtaining humic acids and biochars consisted of two stages:

I. Obtaining humic acids by alkaline extraction
II. Obtaining biochars from solid post-process residues.

As part of the dissertation, the following were conducted:

- Physicochemical examination of peat and brown coal as raw materials to obtain humic substances. Moisture, ash, C, H, N, S, O contents were determined.
- Studies on humic acids extraction processes from peat and brown coal with NaOH and $NH_3 \cdot H_2O$ solutions. The performed experiments aimed to compare isolating methods of humic acids using the method based on the IHSS procedure and the method developed for functional humic preparations described in the patent PL 241814. Analysis of the results allowed for selection of the modification for further studies, in which $NH_3 \cdot H_2O$ solutions were used as extractants and H_3PO_4 solution was proposed as an acidifying agent.
- Investigation of the impact of technological parameters on the efficiency of humic acids obtained from peat and brown coal using $NH_3 \cdot H_2O$ solutions according to the developed modification. Research included an experiment matrix of 15 experimental points for each raw material. The Statistica software version 13.3 was used in the design of experiments. The effects of three independent variables were investigated: extractant concentration, extraction time and extraction temperature. The performance of the system was defined as the efficiency of humic acids obtainment referring to the weight of the raw material used. Research results were illustrated by response surface plots with contour plots. The optimal

process parameters were determined: for peat the concentration of $NH_3 \cdot H_2O$ solution was equal to 0.38 $mol \cdot dm^{-3}$, extraction duration 215 min, extraction temperature 63°C and for brown coal the concentration of $NH_3 \cdot H_2O$ solution 0.37 $mol \cdot dm^{-3}$, extraction duration 206 min, extraction temperature 64°C.

- In order to manage the post-process residues of the peat and brown coal obtained in the modified method of extraction of humic acids with $NH_3 \cdot H_2O$ solutions, developed in this PhD thesis, studies were conducted on the possibility of producing biochars from these residues. The experiments used residues from extraction processes conducted under predetermined optimum conditions. The biochar preparation was performed in the Department of Physical Chemistry of Porous Materials of the B. Dobrzański Institute of Agrophysics of the Polish Academy of Sciences in Lublin. The choice of the institute was driven by scientific cooperation based on joint experiments on humic acids and the use of biochar in agriculture. Pyrolysis processes were performed at three temperature variants: 300, 450 and 600°C.

The summary of the research work involved developing preliminary, simplified concept for obtaining humic acids from peat and brown coal using $NH_3 \cdot H_2O$ solutions according to a modified extraction method, assuming the optimal conditions, as well as biochar technology based on post-process residue obtained under these conditions. The assumed efficiency of humic acids obtained was 34% when using peat as raw material and 29% when using brown coal. A pyrolysis temperature of 300°C and a biochar production efficiency of 70% were assumed. The characteristics of the potential products obtained according to the proposed concept were also developed.

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