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Application of microwave-assisted extraction for the intensification of humic acid isolation from peat

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Abstract
Humic acids (HAs) are components of natural organic matter found in soil and are considered responsible for its fertility. They can be extracted from sources such as peat and lignite on an industrial scale. In order to increase the efficiency and reduce the duration of the alkaline extraction step, microwave-assisted extraction (MAE) was used in this study. Statistical analysis was implemented to describe the influence of microwave power, temperature, and time on the yield of HA extraction. Experimental points were created on the basis of the matrix, according to the Box–Behnken design. Statistical analysis showed the importance of linear correlations between the process parameters and the response. The last part of the presented study was to create the polynomial model and response surface plots, attached in poster form, which describe the result as a function of parameters of the MAE process.

Keywords
peat, humic acids, microwave-assisted extraction, process intensification, Box–Behnken design

1. INTRODUCTION

Humic substances (HSs) are a complex mixture of naturally occurring substances that can be extracted from soils and sediments. Moreover, important sources of these macromolecular compounds are peat, leonardite, and lignite. HSs differ in structure, size, and solubility. The last property mentioned is used to extract and separate fractions of humic substances (Bondareva and Kudryasheva, 2021; De Souza and Bragança, 2018; Stevenson, 1994; Yakhin et al., 2017).

For the isolation of humic acids (HAs), alkaline solutions, chelating agents, organic solvents, and aqueous salt solutions may be used as extractants. The most commonly used are sodium hydroxide and potassium hydroxide, usually at a concentration in the range of 0.1–0.5 M (Baglieri et al., 2007; Bambalov, 2020; Hayes and Clapp, 2001; Stevenson, 1994; Tatzber et al., 2007). According to the recommendation of the International Humic Substances Society (IHSS), the alkaline extraction of humic substances from natural solid raw materials should be carried out by mechanical shaking in 4 hours. However, using modern extraction methods, such as ultrasound-assisted extraction (UAE) or microwave-assisted extraction (MAE), it is possible to obtain a similar isolation efficiency of HSs with significantly shorter process time, compared to the traditional shake extraction method (Nieweś et al., 2022; Saito and Seckler, 2014).

The aim of the presented study was to determine the influence of MAE process parameters on the efficiency of humic acid isolation from peat using statistical modelling based on the Box–Behnken design (BBD). The detailed impact of process parameters on the results was examined by the use of response surface plots (RSPs) and a polynomial model, which was created based on the results of the statistical assessment of MAE results.

2. MATERIALS AND METHODS

For the obtaining of HAs, peat that was collected from the mouth of the Vistula River was used as a raw material. HAs were extracted in the microwave-assisted alkaline process. It was carried out with the use of an RM-800 microwave reactor (Plazatronika, Wrocław, Poland) and 0.1 M NaOH was used as an extractant. The procedure for HAs isolation from peat using the MAE process consisted of several steps. First, the peat was air-dried and ground into 2 mm particles. Next, the raw material was placed in an Erlenmeyer flask and the extractant was added at a mass ratio of 10:1 to the dry weight of the peat used for extraction. The microwave-assisted alkaline extraction step was carried out at different microwave power, time, and temperature values, according to the experimental points created on the basis of the Box–Behnken design. Each of the three independent variables evaluated in the MAE process was coded at three levels (–1; 0, and 1). After the MAE step, the mixture was separated from the solid residue of the raw material by centrifugation at 1900 rpm for 15 minutes. Then, the supernatant was acidified to a pH below 2 for the precipitation of HAs. The gel of HAs was obtained by collecting them on filtration paper and drying to a constant mass in a laboratory dryer at 105 °C. The powdered HA obtained was incinerated to a constant mass in a muffle furnace at 650 °C.

As a result, for each experimental point, the yield of HA extraction was determined as the mass of HAs isolated from the raw material in relation to the mass of peat in the dry ash-free basis (daf). It was calculated using Equation (1), where HAs^{daf} is the yield of isolated humic acids in the dry ash-free basis, mass%, m_A, m_B, and m_C is the mass of HAs after drying, g, the mass of ash after HA incineration, g, and the mass of raw material used in the extraction process, g, respectively. M means the moisture content of the peat, mass%, and A is the content of the peat ash, mass%.

$$\mathrm{HAs}^{\mathrm{daf}} = \frac{10\,000 \cdot (m_A - m_B)}{m_C \cdot (100 - M - A)} \tag{1}$$

3. RESULTS

The application of the Box–Behnken design for the statistical evaluation of the influence of three independent parameters of the MAE process on the efficiency of HA isolation from peat was associated with the conducting of 15 experiments. For the statistical analysis,

a quadratic model was chosen that includes linear interactions between independent variables. The analysis of results allowed to select parameters that were statistically significant for the response. This allowed us to determine the polynomial model that describes the dependencies between the microwave power, X_1, temperature, X_2, and time, X_3, values and the extraction yield of HAs in the MAE process, Y. It was presented as Equation (2), and refers to the coded values of independent variables, which were statistically significant for the result. For that case, it was assumed that the significant parameters were characterised by a p-value lower than 0.05. On this basis, it can be concluded that the linear and quadratic effects of microwave power, X_1 and X_1^2, temperature, X_3 and X_3^2, as well as the linear interactions of time and microwave power, $X_1 \cdot X_2$, microwave power and temperature, $X_1 \cdot X_3$, and time and temperature, $X_2 \cdot X_3$, had a significant effect on the yield of HA extraction from peat.

$$Y = 14.33 + 1.08 \cdot X_1 + 0.80 \cdot X_1^2 + 2.10 \cdot X_3 - 2.00 \cdot X_3^2 + 0.68 \cdot X_1 \cdot X_2 - 0.93 \cdot X_1 \cdot X_3 + 1.18 \cdot X_2 \cdot X_3 \tag{2}$$

4. CONCLUSIONS

Modern extraction techniques may be an alternative to traditional natural product isolation processes. The aim of the presented study was to apply microwave-assisted extraction (MAE) for the isolation of humic acids (HAs) from peat. On the basis of the presented results, it may be concluded that MAE may be considered a promising method for HA isolation. The statistical analysis, based on the results for the experimental points created according to the Box–Behnken design, showed the significance of most parameters examined for the efficiency of the process. The results of the effect estimates for the parameters of the quadratic model with linear interactions between independent parameters pointed out the negative effect of high temperature, as well as connection of high temperature with high microwave power, on the efficiency of HA extraction from peat in the MAE process.

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SYMBOLS

A	ash content, mass%
HAs	humic acids
HSs	humic substances
IHSS	International Humic Substances Society
M	moisture content, mass%
m_A	mass of humic acids after drying, g
MAE	microwave-assisted extraction
m_B	mass of ash after incineration of HAs, g
m_C	mass of raw material (peat) used in the extraction process, g
RSPs	response surface plots
UAE	ultrasound-assisted extraction
X_1	microwave power, W
X_2	time, min
X_3	temperature, °C
Y	extraction yield of humic acids in the microwave-assisted extraction, mass%

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Intensification of microwave-assisted humic acids extraction from peat

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INTRODUCTION

Humic substances are well known organic molecules with various applications: main components of plant fertilizers and plant growth regulators. Thanks to their antibacterial, detoxifying, antioxidant, antiviral, and anti-inflammatory properties humic acids and fulvic acids are considered as promising medicines and drug solubilizer and carrier [1].

Conventional extraction of humic acids is based on mechanical mixing with the extractant. Its advantages include the simplicity and relative low cost of the process. The biggest disadvantage, on the other hand, is the duration of such extraction, which is up to 24 hours [2].

With the use of modern methods of assisted extraction, such as microwaves (MAE) or ultrasound (UAE), it is possible to significantly reduce the extraction time and, with the right choice of parameters, also increase its efficiency [3].

OBCJECTIVE

Determine the **effect of basic extraction parameters**, such as **time and temperature**, combined with **microwave power**, on the **efficiency of obtaining humic acids**.

METHODS

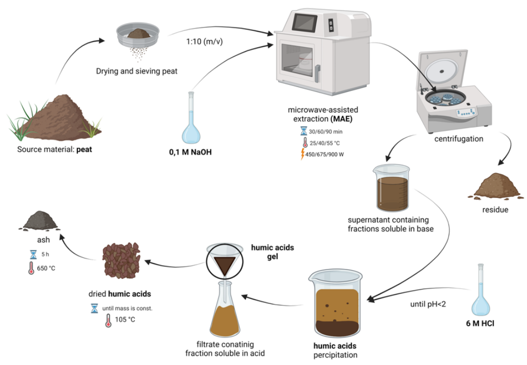

Figure 1. Methodology of humic acids extraction.

Humic acids were obtained by **microwave-assisted extraction (MAE)**. The extractant that was used was **0.1 M NaOH** added at a ratio of **10:1** to the dry weight of the **peat** used for extraction. **Yield** was defined as the mass of dry, ash-free humic acids per dry, ash-free raw material. **Statistical analysis** was used to determine the effect of microwave power, extraction time, and temperature on the yield of humic acid. More detailed methodoldgy can be seen in figure 1.

The **Box–Behnken statistical design** was employed as a screening method to study the effects of different variables affecting the extraction process such as extraction temperature, extraction time, and power of microwaves. In the Box–Behnken statistical design, all the factors chosen were of numeric type and continuous subtype with **low level (–1), medium level (0) and high level (+1)**. Examined parameters of time, temperature and ultrasound power are shown in table 1.

Table 1. Description of the independent variables with levels

Factor	Name	Unit	Low level	Medium level	High level
A	Extraction temperature	Degree °C	25	40	55
B	Ectraction time	Minutes	30	60	90
C	Power of microwaves	Wat	450	675	900

RESULTS

Temperature is an important factor influencing extraction efficiency, which is also supported by the findings of other researchers [3]. The same observation applies to extraction time. The higher both factors are, the higher the efficiency of the process, as graphically shown in the response surface plot AB.

Increasing microwave power negatively affects the efficiency of the process. Experimental results suggest that it is better to run the process using microwaves with low power but at a higher temperature.

Regarding the relationship between microwave power and extraction time, potentially high efficiency can be achieved in two ways: using low power and short extraction or increasing power and increasing process time. For economic reasons, the former is more advantageous.

3D Surface Plots were generated to access how the response varies as a function of the two factors chosen. The graphs between AB, AC, and BC were plotted to closely monitor the effect on humic acids yield and are shown in figures 2-4.

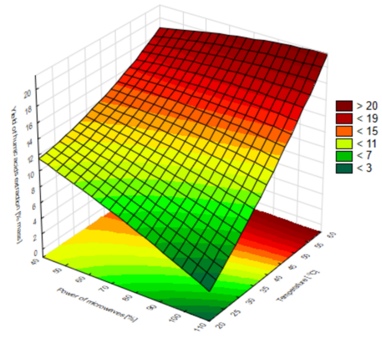

Figure 2. Response surface plots between the factors AC

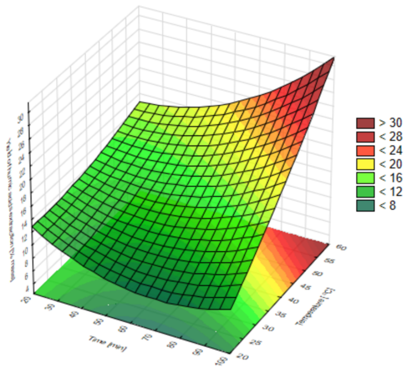

Figure 3. Response surface plots between the factors AB

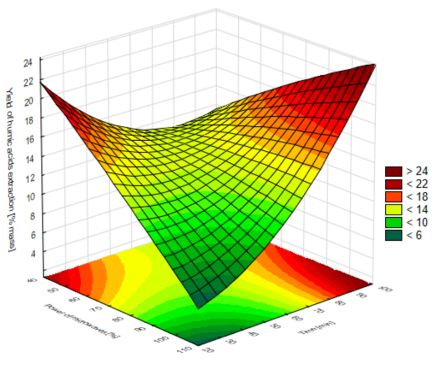

Figure 4. Response surface plots between the factors BC

CONCLUSION

- Statistical analysis makes it possible to determine the trend of the studied process and suggest a direction for further research.
- MAE can be considered as a new and fast method of extraction for humic acid.
- Increasing temperature increase yeild of humic acids in every conditions.
- MAE conducted with high temperature, low time and low microwaves power may be most efficient.
- Based on the results obtained, it will be possible to develop a process equation depending on the independent variables, which in turn will make it possible to intensify the process.

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