Evaluation of the removal potential of fulvic acids after ultrasound assisted extraction of humic substances from peat

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ABSTRACT

One of new emerging research areas is related to an anthropogenic humic-like and fulvic-like matter, released from fertilizers into the aquatic environment, which presence in treated water leads to a generation of disinfection and oxidation by-products of mutagenic and carcinogenic character that may cause additional technological difficulties. These problems can be already solved at the stage of humic and fulvic acids production. The aim of the present work was to assess the impact of ultrasounds on the extraction efficiency of humic compounds from peat and hydrophobicity of obtained fulvic acids fraction which has the greatest impact on the subsequent water purification process. The hydrophobic character of the fraction adsorbed to DAX-8 resin was confirmed by differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA–TG–MS). Ultrasound assisted extraction (UAE) allows to obtain almost four times more humic acids – 57.3 wt.% from a given mass of raw material than during the use of a method without ultrasounds. Generally, fulvic acids extracted from peat using traditional method consist of similar amounts of hydrophobic fraction and this, which is characterized by non-humic structure and because of greater affinity for water (hydrophilic) making its removal more difficult. During UAE, about 70%–75% of hydrophobic fulvic acids were obtained.

Keywords: Fulvic acids; Adsorption; Ultrasounds; DAX-8 polymer resin

1. Introduction

Purification of water containing humic substances creates technological problems and is practically impossible to achieve by applying traditional groundwater treatment processes. The most problematic fraction are fulvic acids. The term fulvic acids (FA), just like humic acids (HA) and humin does not refer to discrete chemical compounds but include a wide variety of compounds of varying molecular weight, solubility, degree of polymerization, and color. It is believed that fulvic acids have less aromatic but more acidic character than humic acids [1–3]. From a chemical point of view, these compounds can be generally described as molecules consisting of aromatic, organic polymers with many functional groups [4–6]. Because of the fact that FA have a more aliphatic character, are smaller and have higher solubility in water, they are much more chemically reactive than HA [7,8]. Therefore, the fulvic acids fraction can form soluble complexes with metals and hydrophobic organic substances and thus lead to their mobilization in soil and water environments [1,2,9–12].

Chemical and physical characteristics of fulvic acids are strongly dependent on a source of their origin

– environmental conditions under which they were formed. These compounds are considered among the most important components of natural organic matter (NOM) in terrestrial and aquatic ecosystems as well as in geological deposits. Organic matter in the ecosphere is originated also from anthropogenic inputs as additional sources of humus compounds [1,13].

The use of humic and fulvic acids is a common practice in agricultural in form of fertilizers and soil additives. Increased production and continuous expansion of the range of such products have been ones of the main trends on fertilizer market [14,15]. The chemical structure of humus compounds and contents of reactive functional groups enable to obtain mineral-organic linkages of different kind, which have influence on mobility of metal ions in the soil and, in consequence, increase the efficiency of mineral fertilizers effects [16–20]. However, because of high activity and solubility of fulvic compounds, their occurrence is not only limited to soil ecosystems, but may be leaching out to surface waters and subsequently to the groundwater. Therefore, these features, which indicate the beneficial use of fulvic acids in agriculture, can simultaneously affect wastewater treatment process in an adverse way. Dangerous fact is that fulvic acids can cause by-products formation after chemical disinfection and therefore can be considered as precursors of carcinogenic and mutagenic trihalomethanes (THMs) [3,21–24]. Another well-known effects of fulvic acids presence in water and wastewater are color, taste, and odor problems [25]. The coexistence of humic substances and iron in groundwater causes an occurrence of a specified part of iron in a form of iron-organic bounds. As a result, water has an increased color and turbidity, which is problematic in the technological aspect for efficient treatment [3]. Therefore, an introduction into the ecosystem of a commercial product containing fulvic acids has a double meaning in terms of generalized transformations occurring within it. Chemical and physical properties of humus preparations depend primarily on source of their origin. Humic substances (HS) are sourced not only from soil but also from compost, manure, biosolids (sewage sludge), peats, coals such as lignite and particular oxidized lignite – leonardite [18,19,26].

An another factor influencing the chemical character of the obtained humic and fulvic acids, as well as the efficiency of their extraction from potential organic sources, is the isolation procedure [4,6,19].

Production of commercial humic and fulvic acids is based on a "classical" procedure for extracting these fractions from soil described in detail by Stevenson [1] and modified by many scientists, that is, Swift [27] and Waksman and Humus [27,28].

These methods differ in the type and concentration of extractant, time, and temperature of extraction as well as technique of proceeding etc. In the process of obtaining humic substances, ultrasound assisted extraction (UAE) or microwave assisted extraction (MAE) are often used. This allows obtaining a similar amount of humic substances from a given mass of raw material in a much shorter time [29–31].

It is important to stress that the production process of humic substances from alternative organic materials on an industrial scale is primarily aimed at obtaining a solid humic fraction with sufficiently high efficiency. The fulvic fraction obtained after phase separation is a kind of a valuable by-product.

The aim of present examinations was the assessment of using UAE for preparation of humic and fulvic acids from peat and then the determination of the impact of process parameters on the possibility of fulvic acids removal. Efficiency of humic and fulvic acids yield in traditional extraction and UAE were compared. In the ultrasonic field of sufficient intensity to induce cavitation, the effects of mechanical degradation of macromolecular compounds are observed, which may support subsequent sorption of fulvic acids from obtained solution. UAE for preparation of humic and fulvic acids from peat was carried out with variables in form of ultrasounds power and time of extraction.

The hydrophobicity of NOM has a major control on water treatment. One of methods for the separation of organic compounds is the method using the phenomenon of adsorption of individual NOM fractions on DAX type non-ionic macroporous synthetic resins. This method has been repeatedly modified by a number of researchers, and is mainly based on the adsorption of individual NOM fractions depending on their solubility and hydrophobicity [5,9,15,32–35]. Therefore, the use of adsorption resins is particularly suited to identify removal potential. HPO species are readily removed from solution by the traditional coagulation method, while HPI species remain in solution and pass through to the final effluent [36].

In the present study, the adsorption process of obtained fulvic acids from two methods of extraction was carried out on a DAX-8 polymer resin. For desorption, a 0.1 mol/dm^3 NH$_3$ solution was passed through the bed. The fraction adsorbed on the DAX-8 and then desorbed in alkali solution is referred to as a hydrophobic fraction – HPO while hydrophilic fraction (HPI) passes through the resin into effluent. Different fractions are characterized by different functional groups. Aromatic phenol groups are more commonly associated with the HPO fraction. The HPI fraction contains more aliphatic and carboxyl carbons and nitrogenous compounds such as low molecular weight carbohydrates, proteins, and amino acids [37–39].

The assessment of the impact of ultrasounds on the effectiveness of fulvic acids adsorption on a polymer resin and consequently the possibility of their removal was made on the basis of the concentration of fulvic acids in eluate and on their properties (before and after adsorption on resin) evaluated by thermal analysis. Measurements were performed with the use of differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA–TG–MS).

2. Materials and methods

The raw material used in the process of obtaining humic and fulvic acids by ultrasonic assisted alkaline extraction (UAE) was peat from the mouth of the Vistula. The moisture content of the tested peat material was high and averaged 85.0 wt.%. The content of organic matter was on average 76.5 wt.% and the average ash content was 23.5 wt.% of dry matter.

2.1. Procedure of humic and fulvic acids extraction

For the extraction of humic and fulvic acids from peat, analytical techniques that are typically applied in studies of soil organic matter, as well as in patent descriptions related to commercial products, were used.

Before extraction, peat was first subjected to pretreatment with hydrochloric acid to remove calcium and other polyvalent cations and thereby increase the efficiency of humic and fulvic acids extraction. For this purpose, a peat sample was mixed with a 1 M HCl solution until a pH of 1–2 was obtained. Then, 0.1 M HCl was added so that there was 10 cm³ of liquid per gram of raw material and the mixture was shaken for 1 h at room temperature. After that time, peat was separated from the solution by centrifugation and neutralized with 1 M NaOH to pH 7.0.

The extraction of humic and fulvic acids from peat was carried out using two methods: a traditional method (TM) and with the use of ultrasounds (UAE method). Regardless of the method, procedure of extraction involves two stages. In the first step, peat was treated with 0.5 M NaOH (1:15 w/w) by constant stirring in a laboratory shaker (TM) or sonicated in ultrasonic bath Emmi 40 HC (UAE), both at room temperature. The extraction was carried out in two process times: 15 and 45 min in three series, with 15 min intervals between them without shaking in TM or without ultrasounds in UAE. UAE for preparation of humic and fulvic acids from peat was carried out with the use of two ultrasounds powers: 50 and 100 W and a frequency of 45 kHz.

In the second step, regardless of the method the mixture was centrifuged at 3,000 × g for 10 min and the soluble supernatant (humic substances – HS) was separated from the insoluble sediment (humin). In the second stage HA were precipitated from the extract by acidification of the environment by adding 2 M H_2SO_4 solution to pH 2.0. The coagulation lasted 24 h. Afterwards, HA were separated from the soluble fulvic acids (FA) by centrifugation, as described above.

Efficiency of humic acids yield in traditional and UAE were compared. For this purpose, the ash-free mass of HA after precipitation, drying, and ashing was determined. The amount of humic acids extracted in individual processes was determined by the gravimetrical method, which is a modification of the method described in the standard PN-89/G-97051.16. Content of humic acids for dry and ash-free state (HA^{daf}) was expressed in wt.% and calculated according to the following formula [40]:

$$HA^{daf} = \frac{10,000 \cdot (m_1 - m_2)}{m_3 \cdot (100 - W_1^a - A_1^a)} \cdot \frac{V_0}{V_1} \qquad (1)$$

where m_1 is the mass of dried humic acids (g), m_2 is the mass of the residue after ashing the sample at 615°C (g), m_3 is the weight of input peat sample (g), V_0 is the total volume of the alkaline solution (cm³), V_1 is the volume of the solution collected for examination of humic acids (cm³), W_1^a and A_1^a are the moisture and ash content in the peat analytical sample, respectively (wt.%).

2.2. Fulvic acids DAX-8 adsorption procedure

The fulvic acids adsorption process was carried out on a DAX type non-ionic macroporous synthetic resins. The resin used in the study was Supelite™ DAX-8 from Sigma-Aldrich (St. Louis, Missouri, USA), which was prepared in accordance with the manufacturer's instructions. Collected samples of fulvic acids after traditional and UAE were passed through a column of resin at a flow rate of 15-bed volume/h. The column volume was adjusted to the ratio of 0.15 mL to 1 g of the initial peat sample. The non-adsorbed fraction of FA was discarded. For desorption, a 0.1 mol/dm³ NH₃ solution was passed through the bed.

In the present study, the term hydrophobic FA refers to fraction adsorbed to a hydrophobic resin at acidic pH conditions and which is more hydrophobic than the non-adsorbed fraction that remained in the eluate – called hydrophilic FA. The assessment of the impact of the extraction method (with or without ultrasounds) on the subsequent effectiveness of fulvic acids adsorption on a polymer resin and consequently the possibility of their removal was estimated on the basis of the concentration of fulvic acids in obtained fractions. The content of hydrophobic and hydrophilic FA was expressed as a percentage of organic carbon content C_{org} in these fractions and was determined using Alten's method.

2.4. DTA–TG–MS analysis

In order to assess the impact of ultrasounds on the obtained fractions of fulvic acids – before and after the adsorption on resin – thermal analysis was used. The fraction of FA before adsorption on resin refers to FA which was obtained during the extraction process and, in the present study, is referred to as FA. The fraction of FA after adsorption on resin refers to hydrophobic FA (HPO FA) which was adsorbed to DAX-8 and desorbed in alkali solution.

Measurements were performed with the use of differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA–TG–MS). Before measurement, tested fractions were concentrated with a vacuum evaporator and dried at a temperature lower than 50°C to get a FA samples in form of powder.

A thermal analyzer STA 449 F3 Jupiter® with a thermobalance and a quadrupole mass spectrometer QMS 403 Aëolos®, Netzsch, were used. The equipment was previously calibrated to ensure that correct results were to be obtained. Heating rate was set to 5°C·min⁻¹ in the temperature range of 35°C–850°C and synthetic air with a 30 mL min⁻¹ total flow of the purge gas. Thermogravimetric curves were obtained from approximately 30 mg of solid fulvic acids samples with the use of an empty crucible as a reference material. DTA type S thermocouple and Al_2O_3 crucibles with pierced lids were used. In order to detect the gas evolved from the thermal analyzer, selected ion monitoring for mass-to-charge ratios (m/z) consisted of following signals was used: 18 (H_2O) and 44 (N_2O, CO_2).

3. Results and discussion

The efficiency of humic and fulvic acids extraction is determined not only by raw material which are extracted

from or physicochemical parameters of the process but also by technique of proceeding. Using additional treatments in the form of ultrasounds or microwaves can increase efficiency of the process, which is especially important from an economic point of view. The values of parameters of the alkaline extraction process of humic fractions from peat by traditional and ultrasonic methods, as well as results of extraction efficiency of humic acids, are summarized in Table 1.

The largest efficiency of humic acids extraction – 57.3 wt.% was obtained in process with using ultrasounds for the longest duration of the process. In this case, UAE allows obtaining almost four times more humic acids from a given mass of raw material. In both methods, no effect of extraction time on process efficiency was observed. The method of extraction of humic compounds from alternative organic materials, that is used in commercial production, is a primary method for production of solid humic fraction with economically profitable high performance. In this context, the UAE is a very beneficial method for producing humic acids on an industrial scale. An innovative UAE is the rapid non-thermal extraction technique, which in comparison to conventional extraction, offers high reproducibility in a short time with simplified manipulation, reduced solvent consumption, and lower energy.

In this procedure, a fulvic fraction is also received as a valuable by-product. However, an introduction of this kind of compounds into the environment may cause complications in the subsequent purification of water because of their greater solubility and reactivity. The assessment of the impact of extraction method (with or without ultrasounds) on the subsequent effectiveness of fulvic acids adsorption on a polymer resin and, consequently, the possibility of their removal was made on the basis of the concentration of fulvic acids in obtained fractions expressed as a percentage of C_{org} content. Fig. 1 shows the fractionation of fulvic

acids effect using DAX-8 to produce the HPO fraction. The C_{org} remaining in the solution was the HPI fraction.

Generally, fulvic acids extracted form peat using traditional method consist of similar amounts of hydrophobic and hydrophilic fraction. The extraction time was not a critical factor of the percentage fractions distribution. The obtained results may suggest that a longer process time leads to extraction of a larger amount of hydrophilic fraction. This fraction partially consists of non-humic substances (i.e., polysaccharides, amino sugars, amino acids, proteins, fatty acids, carbohydrates, lipids, etc.) which, from the extraction process point of view, artificially increase the amount of proper fulvic acids. This observation is connected with the fact that stronger conditions of humic substances extraction cause extraction of additional substances present in raw material.

Comparing results depending on method of extraction it was noticed that ultrasounds definitely influence the fractional composition of obtained fulvic acids. During UAE, about 70%–75% of hydrophobic fulvic acids were obtained. Understanding of differences between HPO and HPI fractions allows to select the most appropriate water treatment techniques, because there is no single most effective NOM removal method. As a result, HPI fraction causes usually greater membrane fouling, while water containing HPO fraction has higher coagulant demands [41–43]. From treatment water process point of view, presence of HPO fraction is more favorable because of its lower affinity for water and an easier way of its removal. However, it is important to stress that unsaturated HPO functional groups, such as arenes, react more rapidly with chlorine than carboxylic structures more dominating in others fractions and therefore HPO FA are considered to be the main disinfection by-product precursors [44].

For this reason, hydrophobic fulvic acids should be well characterized. The character of these fractions depends

Table 1
Comparison of efficiency of humic acids extraction from peat in traditional (TM) and ultrasound assisted extraction (UAE), respectively, without or with a power of 50 and 100 W using 0.5 M NaOH for 15 or 45 min operation time

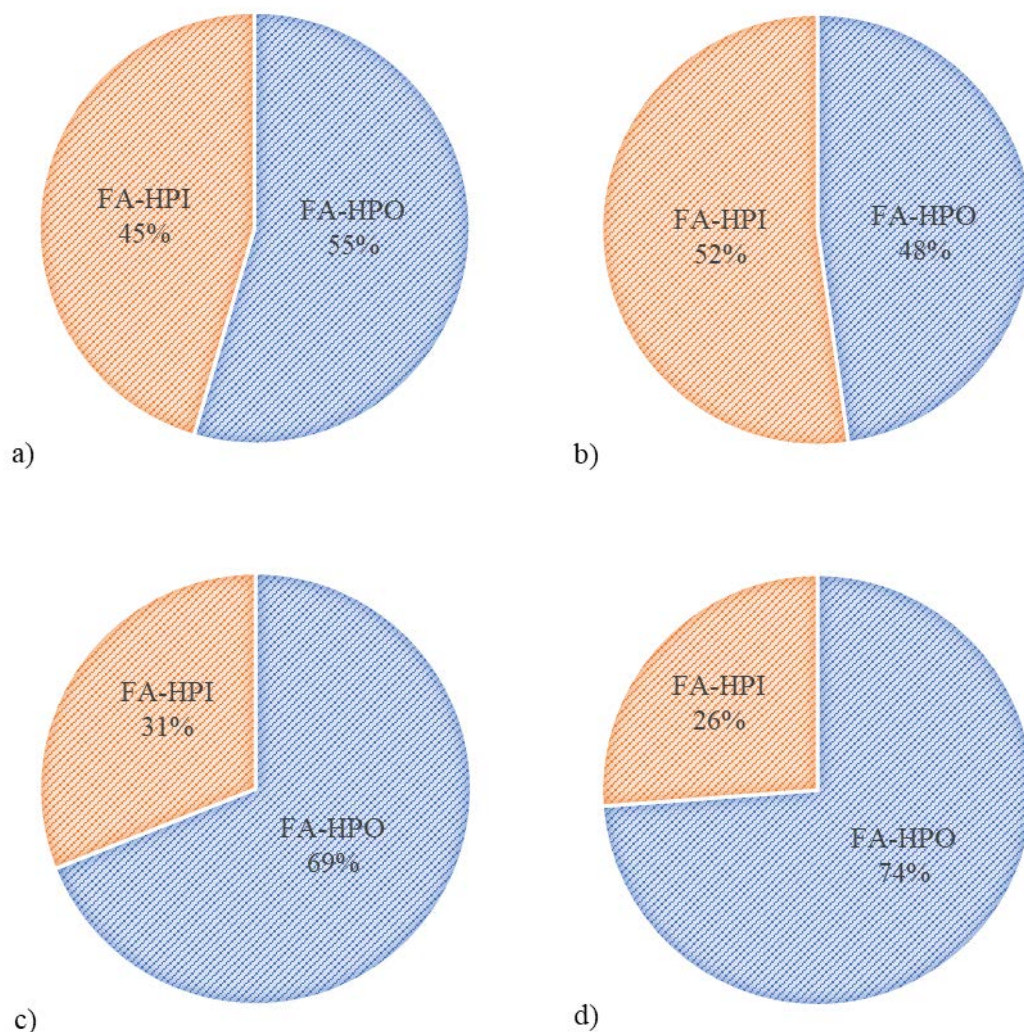| Type of extractant	Concentration of extractant (mol dm⁻³)	Temperature of extraction (°C)	Time of extraction (min)	Mass ratio of extractant and raw material – L:S (w/w)	Method of extraction	Power of ultrasounds (W)	Amount of HA extracted from peat (wt.%)	Average amount of HA extracted from peat (wt.%)
NaOH	0.5	20	15	15:1	TM	–	14.0 15.9 15.7	15.2
					UAE	50	36.9 41.5 38.9	39.1
	0.5	20	45	15:1	TM	–	14.5 15.8 16.5	15.6
					UAE	100	54.4 56.3 61.1	57.3

Fig. 1. Fractional composition of fulvic acids extracted from peat using 0.5 M NaOH in (a) traditional method with a 15 min operation time, (b) traditional method with a 45-min operation time, (c) ultrasounds method with a power of 50 W with a 15 min operation time, and (d) ultrasound method with a power of 100 W with a 45 min operation time.

on, that is, physicochemical parameters of their extraction. Identification of compounds formed during thermal decomposition of fulvic acids and their hydrophobic form was made using differential thermal analysis coupled with thermogravimetry and mass spectrometry as crucial factors to determine their environmental behavior.

It can be distinguished that FA, for which significant loss mass in the lower temperature range is observed, have less condensed structures with aliphatic character and carboxyl groups. Peaks shift toward a high temperature means that fulvic acids are characterized by more thermally stable structure as is the case of aromatic compounds.

The thermal analysis of fulvic acids samples were carried out in conjunction with the identification of gaseous decomposition products by mass spectrometry. Changes in CO_2 content ($m/z = 44$), H_2O ($m/z = 18$), which were observed during heating of the samples, were indicated on the thermograms.

The shape of TG/DTA curves for initial fulvic acids samples (after extraction and before column separation) were

different from their hydrophobic forms independent on extraction method.

On all graphs an endothermic peak in a temperature range of 100°C–120°C was observed. This effect was mainly attributed to the evaporation of water that was physically adsorbed and structurally incorporated into organic particles [45–47]. Analysis of gaseous decomposition products by mass spectrometry for examined samples confirms his transformation by an increase in H_2O release near these range of temperature.

For all examined samples, an intense increase in CO_2 signal can be observed at the temperature ranges of the characteristic exothermic peaks, which confirms the carbon distribution of both an aliphatic and aromatic nature. Results of the thermal analysis of fulvic acids extracted from peat using 0.5 M NaOH by traditional method are shown in graphs 2 and 4, and MS signals for gaseous products created during analysis of these samples in graphs 3 and 5, respectively.

On the TG/DTA curves of FA extracted from peat using traditional method (Figs. 2 and 4), a multistage exothermic
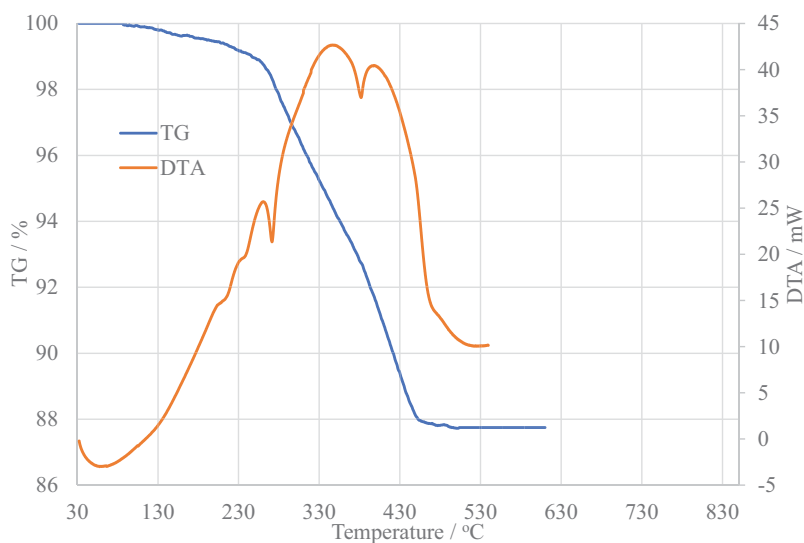
Fig. 2. TG/DTA curves of FA extracted from peat using 0.5 M NaOH by traditional method with a 15 min operation time.
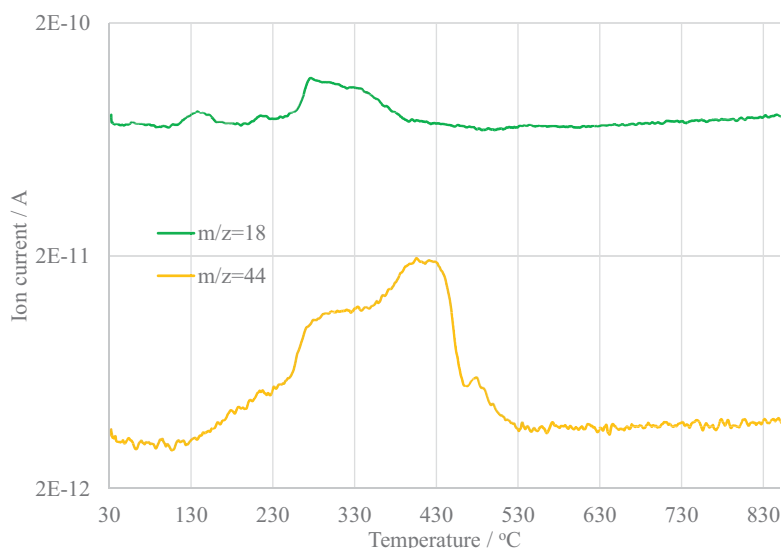

Fig. 3. MS signals for gaseous products created during thermal analysis of FA extracted from peat using 0.5 M NaOH by traditional method with a 15 min operation time.

decomposition of organic substances contained in examined samples from 230°C to 455°C can be observed. These changes indicate the complexity of reactions taking place in the examined sample, which can be interpreted as an evidence of the very diverse composition of obtained fulvic acids. Transformations that occur between 200°C and 350°C are most likely the result of less thermally stable structures degradation – generally characterized by a less condensed structure. The one main change in the DTA graph is reflected in the form of exothermic peaks at a temperature close to 250°C–270°C and correlated mass loss is attributed to decomposition of simple and labile structures, for example, decarboxylation of carboxylic groups. Generally, the intensity of this process was similar for all examined fulvic acids after extraction and before fraction separation independent of

extraction method and lower for hydrophobic FA, what indicates fewer structures with lower bond energy in fraction adsorbed to DAX-8 [47].

This transformation is confirmed by an increased presence of H_2O and CO_2 in a stream of gaseous products (Figs. 3 and 5). The next exothermic effect at a mentioned range occurred at a temperature close to 300°C–330°C and is associated with degradation of carbohydrates and polysaccharides as well as dehydration of aliphatic structures [45,47].

Transformations occurring between 350°C and 455°C and correlated exothermic peaks on DTA curves near temperature of 400°C refer to the degradation of more condensed structures, oxidation of aromatic components and breakdown of C–C bonds in long-chain hydrocarbons. A multistage exothermic distribution of organic substances
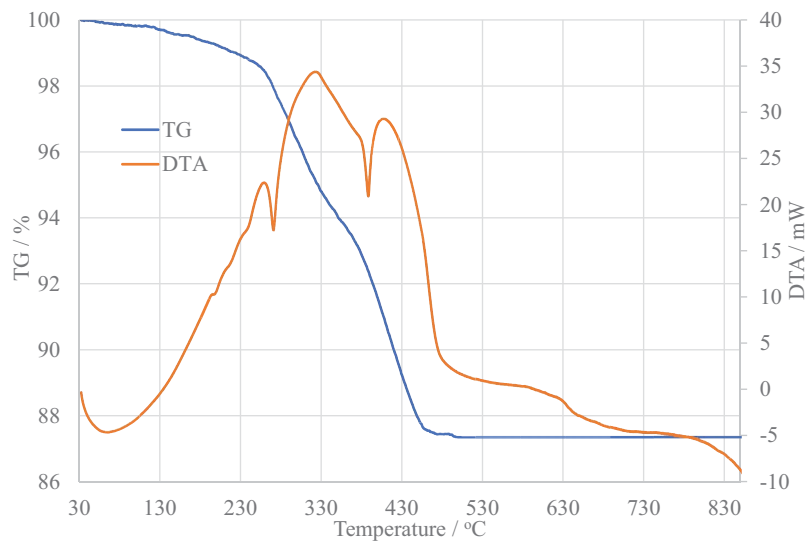
Fig. 4. TG/DTA curves of FA extracted from peat using 0.5 M NaOH by traditional method with a 45 min operation time.
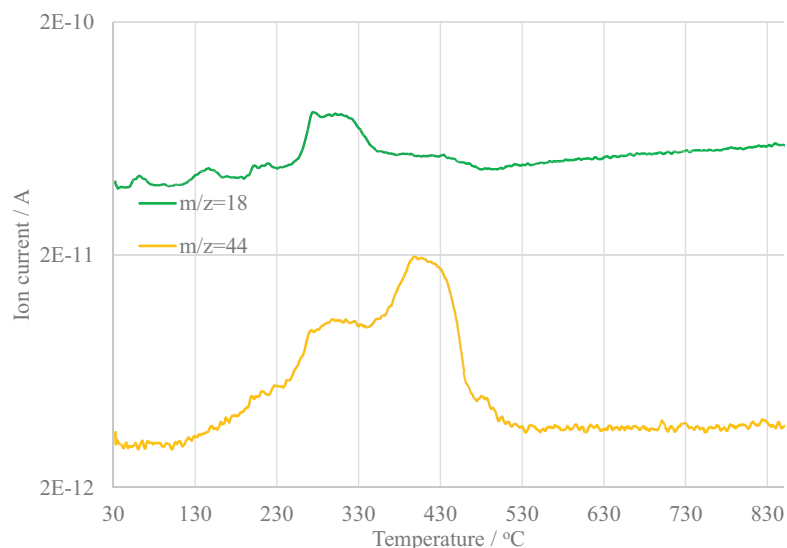

Fig. 5. MS signals for gaseous products created during thermal analysis of FA extracted from peat using 0.5 M NaOH by traditional method with a 45 min operation time.

of fulvic acids obtained from peat by traditional method for a temperature range of 230°C–455°C confirms that these substances contain both hydrophilic and hydrophobic fractions [48–50].

Furthermore, according to the fractional composition of fulvic acids expressed as a percentage of C_{org} content in HPI and HPO fractions, a mass loss indicates that fulvic acids obtained from peat by traditional method independently from extraction time consist of similar amounts of hydrophobic and hydrophilic fractions. For FA extracted by traditional method during shorter process, the loss of mass in a temperature range of 230°C–375°C equal to 6.07 wt.% and in a temperature range of 375°C–455°C was 5.20 wt.%. For FA obtained during longer process the mass loss in a similar temperature range amounted to 4.28 and 6.56 wt.%, respectively.

The results of the thermal analysis of fulvic acids extracted from peat using 0.5 M NaOH by ultrasound assisted method are shown in Figs. 6 and 8, and MS signals for gaseous products created during analysis of these samples in Figs. 7 and 9, respectively.

TG/DTA curves of FA extracted using ultrasounds are characterized by similar transformations as these obtained by the traditional method. The same range of temperature of occurring changes indicates that examined sample also include both HPI fraction containing more aliphatic and carboxyl carbons as well as HPO fraction with more aromatic components. The only exception is the DTA curve of FA extracted using ultrasounds with a power of 50 W with a 15 min operation time, as clear boundaries between mentioned ranges of temperature are not observed. On the
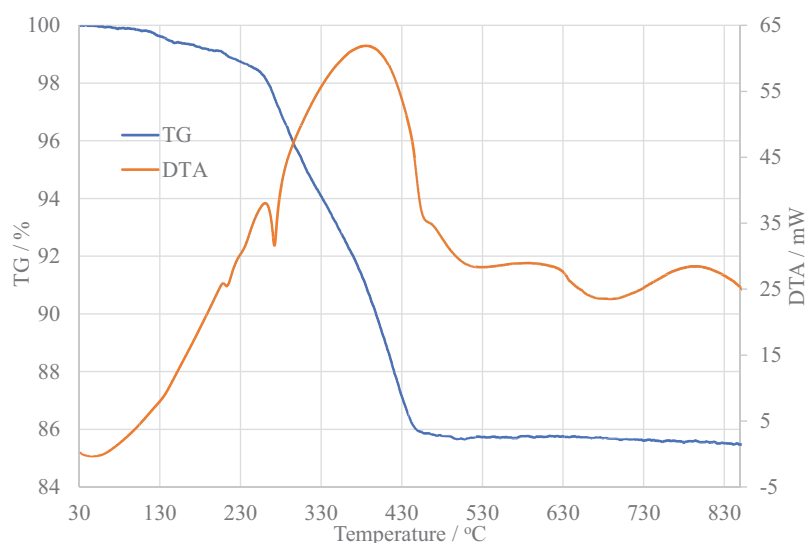
Fig. 6. TG/DTA curves of FA extracted from peat using 0.5 M NaOH by ultrasound assisted method with a power of 50 W with a 15 min operation time.
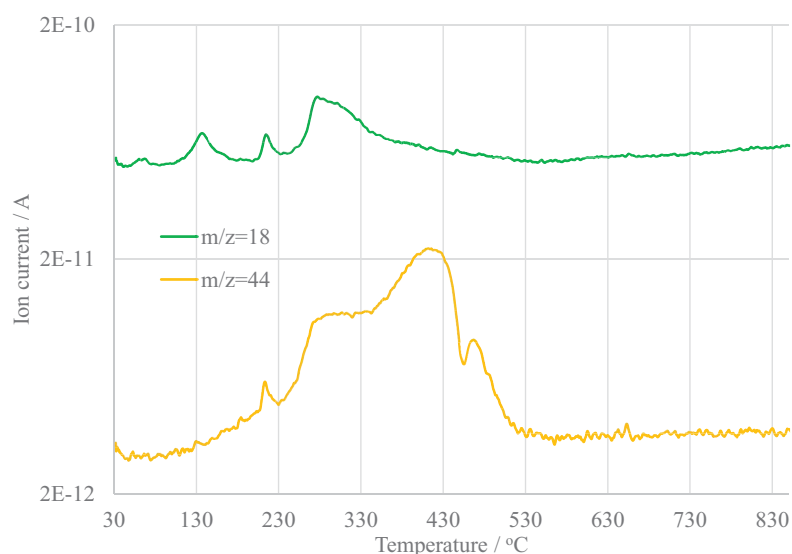

Fig. 7. MS signals for gaseous products created during thermal analysis of FA extracted from peat using 0.5 M NaOH by ultrasound assisted method with a power of 50 W with a 15 min operation time.

shown thermogram (Fig. 6) there is only one large exothermic peak in the temperature range between 220°C and 455°C, accompanied by cumulative 13.0 wt.% mass loss.

However, in the case of above described FA, a 4.36 wt.% loss of mass in a temperature range of 220°C–325°C and a 8.59 wt.% loss of mass in a temperature range of 325°C–455°C indicate that this substance contains more hydrophobic fraction than hydrophilic, what is correlated with results of percentage share of these fractions in sample. Thermal analysis of fulvic acids obtain from peat by UAE with higher process parameter values (50 W, 45 min operation time) are also characterized by a lesser mass loss – 4.89 wt.% in a temperature range of 235°C–335°C which is correlated with HPI fraction

and a greater mass loss – 7.21 wt.% in a temperature range of 335°C–445°C which is correlated with HPO fraction.

It can be expected that FA adsorbed to DAX-8 resin will be characterized by transformations expressed by a DTA peak observed in a higher range of temperature, what is connected with fact that the fraction adsorbed to DAX-8 and then desorbed in alkali solution is referred to as a hydrophobic fraction – HPO.

This is confirmed by the TG/DTA curves of FA adsorbed to DAX-8 resin and previously extracted using traditional method with a 45 min operation time (Fig. 10) as well as extracted using ultrasounds with a power of 50 W with a 15 min operation time (Fig. 12). For these samples, an intense
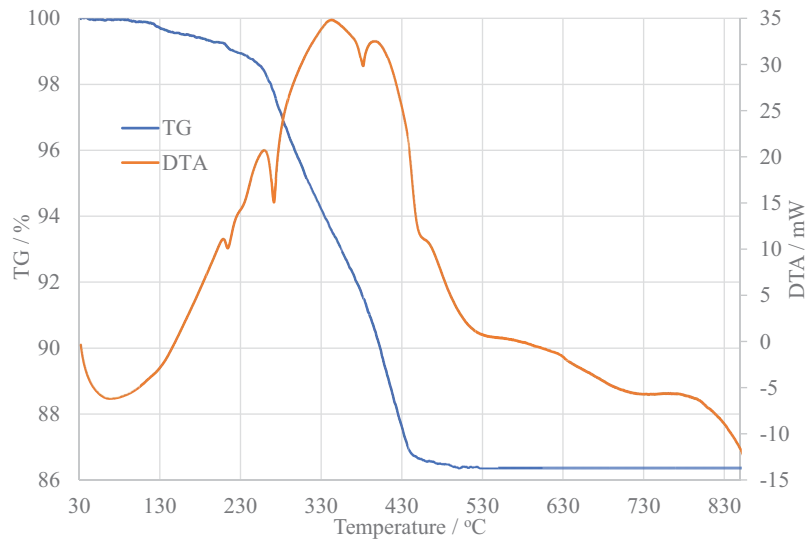
Fig. 8. TG/DTA curves of FA extracted from peat using 0.5 M NaOH by ultrasound assisted method with a power of 100 W with a 45 min operation time.
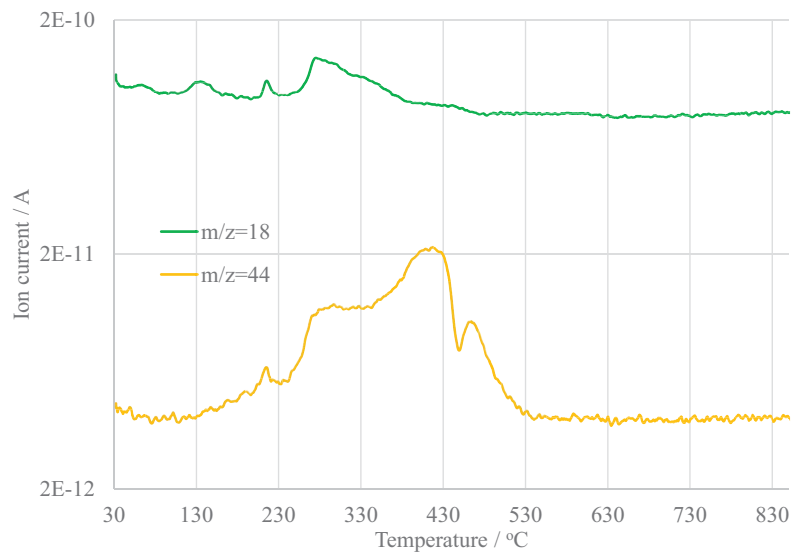

Fig. 9. MS signals for gaseous products created during thermal analysis of FA extracted from peat using 0.5 M NaOH by ultrasound assisted method with a power of 100 W with a 45 min operation time.

increase in CO_2 signal can be observed in the temperature ranges of the characteristic exothermic peaks (Figs. 11 and 13), which confirms the distribution of aromatic carbon structures that are characteristic for HPO fraction.

In both cases, exothermic peaks on DTA curve shift toward a high temperature (450°C–480°C). The temperature range of 430°C–650°C is attributed to a decomposition of N-compounds, long-chain hydrocarbons, as well as cleavage of C–C bonds [47,48]. It means that these fulvic acids are characterized by more refractory, aromatic, polyaromatic, and polyheterocyclic structures. Also, a peak near the temperature of 450°C on the DTA curve of FA adsorbed to DAX-8 resin and previously extracted using ultrasounds with a power of 100 W with a 45 min operation time (Fig. 14)

was observed. Also, on the TG/DTA curves of FA adsorbed to DAX-8 resin and previously extracted using ultrasounds with a power of 100 W with a 45 min operation time (Fig. 14) peak near temperature of 450°C can be observed. Analysis of gaseous decomposition products by mass spectrometry for examined samples also confirm this transformation by an increase of the amount of CO_2 present in the evacuated gasses near this range of temperature (Fig. 15).

On the TG/DTA curves of these adsorbed FA, a second peak near temperature of 590°C can be observed. However, this exothermic effect is not confirmed in the MS analysis as a decomposition of carbon structure and occurred a significant weight loss on TG. This effect may suggest the possibility of aromaticity increasing upon heating that was described
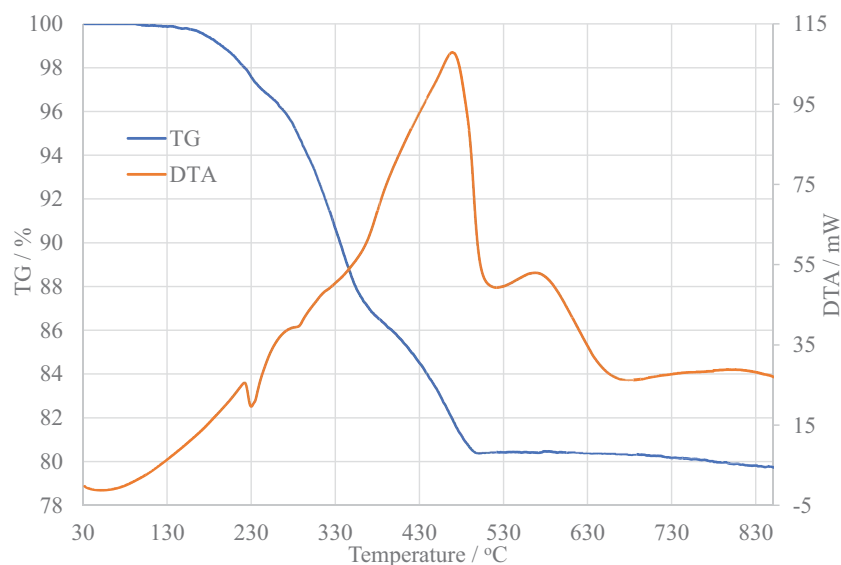
Fig. 10. TG/DTA curves of FA extracted from peat using 0.5 M NaOH by traditional method with a 45 min operation time and adsorbed to DAX-8 resin.
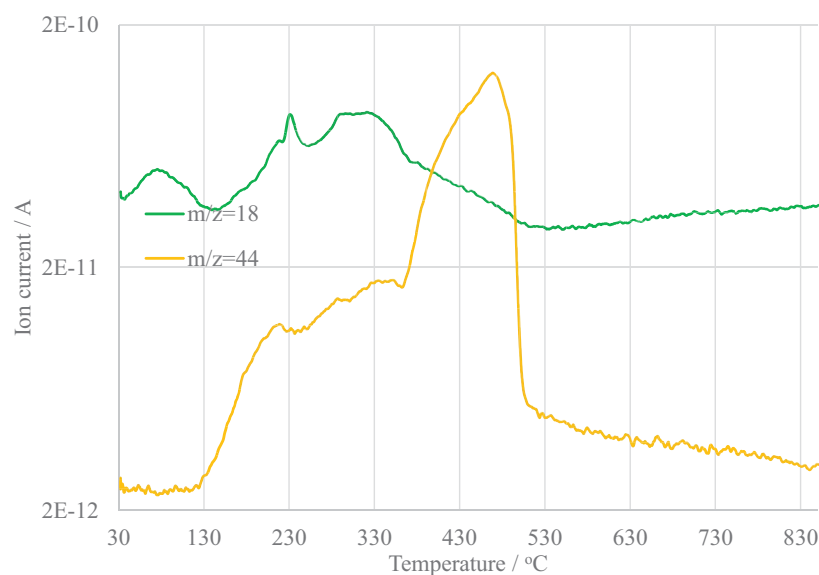

Fig. 11. MS signals for gaseous products created during thermal analysis of FA extracted from peat using 0.5 M NaOH by traditional method with a 45 min operation time and adsorbed to DAX-8 resin.

by Giovanela et al. [45] especially for HA. These scientists stated that such a process could cause a shift of decomposition temperature to the much higher values and thereby it could explain the relatively low weight loss of HAs in 430°C–650°C temperature range. Additionally, Zhang et al. [47] showed that a higher number of long aliphatic chains in HA may cause their condensation to cyclic structures and aromatization upon heating.

From the extraction method point of view, it can suggest that fulvic acids obtained in the ultrasonic process at the assumed parameters are characterized by a higher transformation degree. The process of obtaining humic and fulvic compounds from alternative organic materials should be characterized by such parameters which allow to achieve high efficiency of desired fractions isolation and simultaneously preserve their bioactive structures and obtain products of exceptional quality. Applying more aggressive process conditions for the greater efficiency of the extraction process can be expected, however, there is a risk that it may simultaneously cause partial degradation of structure and contribute to the contamination of the final product with undesirable compounds. On the other hand, less destructive conditions may provide a good quality product at the expense of process efficiency.
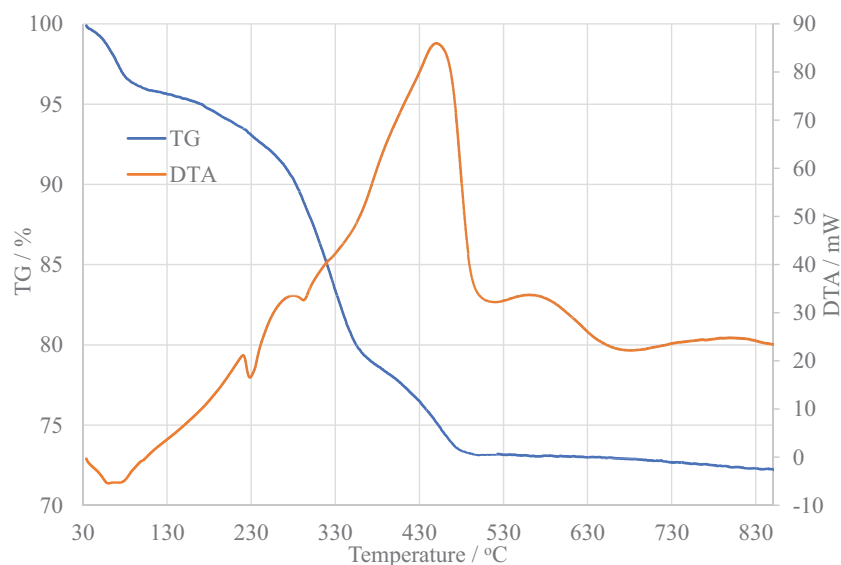
Fig. 12. TG/DTA curves of FA extracted from peat using 0.5 M NaOH by ultrasound assisted method with a power of 50 W with a 15 min operation time and adsorbed to DAX-8 resin.
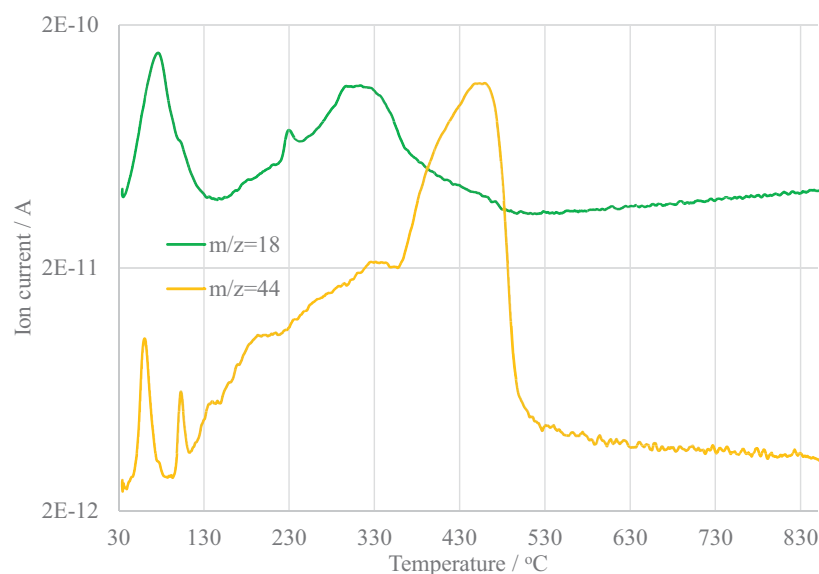

Fig. 13. MS signals for gaseous products created during thermal analysis of FA extracted from peat using 0.5 M NaOH by ultrasound assisted method with a power of 50 W with a 15 min operation time and adsorbed to DAX-8 resin.

The result of the thermal analysis of fulvic acids adsorbed to DAX-8 resin and previously extracted using traditional method with a 15 min operation time is shown in Fig. 16 and MS signals for gaseous products created during analysis of this sample in Fig. 17.

On the shown thermogram there is only one wide multistage exothermic peak in the temperature range between 130°C and 730°C. This kind of organic substances distribution is not observed on any other curves. However, the first exothermic effect, similarly to other adsorbed FA, is observed around 430°C. The further shape of the curve is different from other results and can be caused by endothermic and exothermic effects connected with fusions, decomposition, and polymerizations that occur together as the temperature increases. Changes that are visible in temperatures range of 450°C–545°C may be an effect of a pyrolysis of aromatic components of structures like lignine and other polyphenols. The last visible exothermic effect, in temperatures above 600°C is probably due to high-temperature changes associated with polycondensation and depolymerization reactions [48–50]. Obtained results indicate that fulvic acids extracted using traditional method with a 15 min operation time are characterized by a more condensed structure and contain thermally stable compounds. It should be remembered that
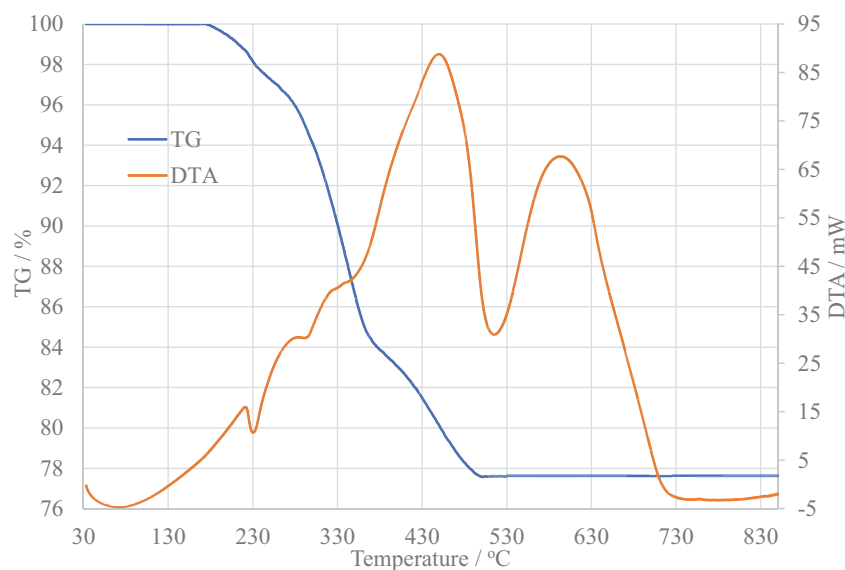
Fig. 14. TG/DTA curves of FA extracted from peat using 0.5 M NaOH by ultrasound assisted method with a power of 100 W with a 45 min operation time and adsorbed to DAX-8 resin.
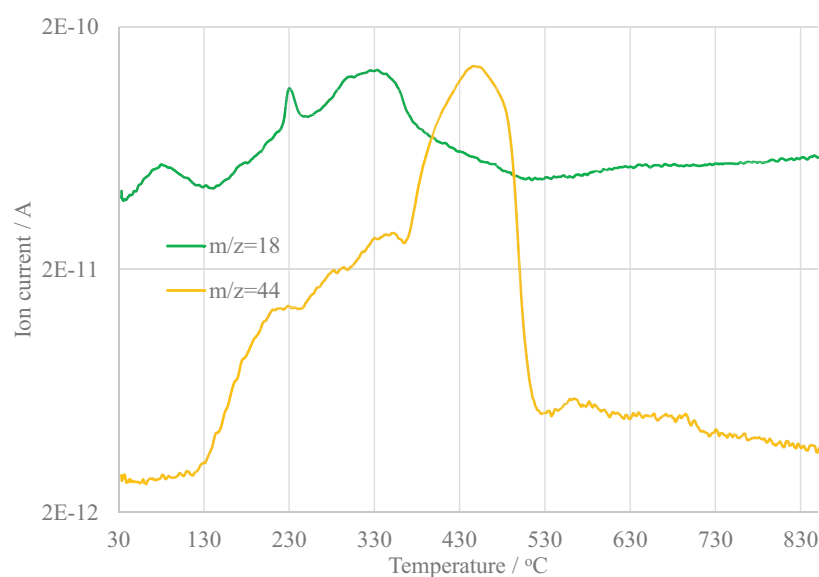

Fig. 15. MS signals for gaseous products created during thermal analysis of FA extracted from peat using 0.5 M NaOH by ultrasound assisted method with a power of 100 W with a 45 min operation time and adsorbed to DAX-8 resin.

the extraction process of examined fulvic acids was characterized by the weakest conditions, which resulted in the lowest extraction efficiency. In the context of water purification, however, this fraction should pose the least problems in removing them.

4. Conclusions

The products currently available on the agricultural market as FA often contain both fulvic fractions – desired hydrophobic and non-humic hydrophilic components that are more troublesome in the subsequent removal from water. Introduction of such preparations into the natural environment can, in consequence, complicate any water treatment processes and, because of potential formation disinfection and oxidation by-products of mutagenic and carcinogenic character, can be dangerous for human health. To reduce the content of FA to the required level, new, effective techniques for their removal are sought. The hydrophobicity of obtained fulvic acids fractions is the most important determinant of the removal potential. This problem can be already solved at the stage of humic and fulvic acids production. The method of obtaining humus compounds from alternative organic materials should be characterized by
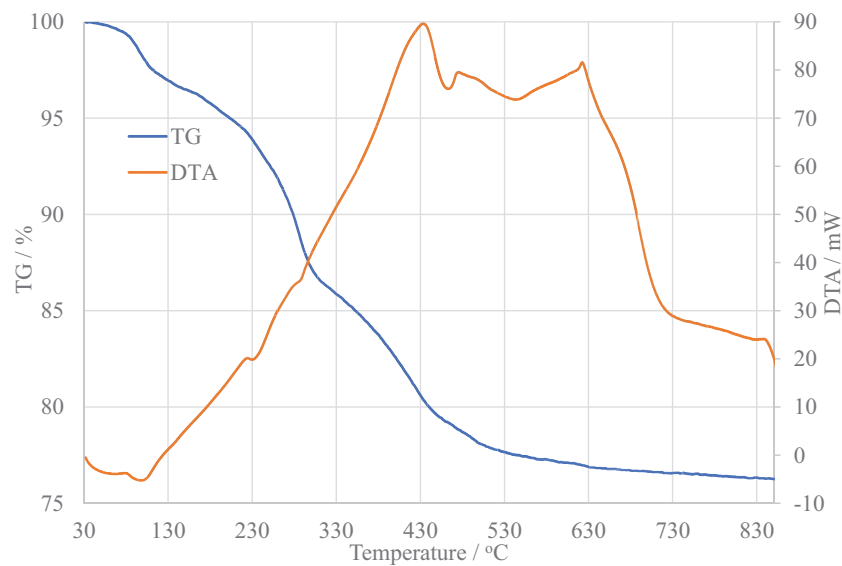
Fig. 16. TG/DTA curves of FA extracted from peat using 0.5 M NaOH by traditional method with a 15 min operation time and adsorbed to DAX-8 resin.
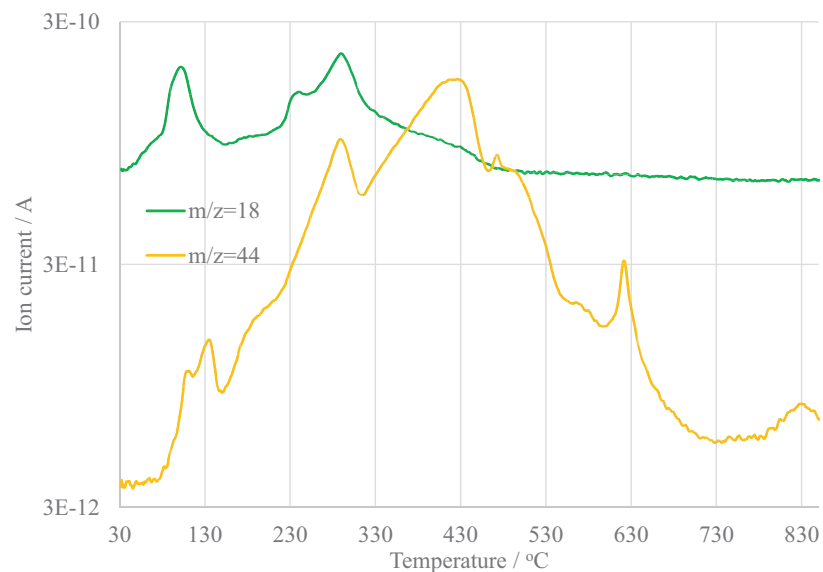

Fig. 17. MS signals for gaseous products created during thermal analysis of FA extracted from peat using 0.5 M NaOH by traditional method with a 15 min operation time and adsorbed to DAX-8 resin.

such parameters which allow to achieve high efficiency of desired fractions isolation and simultaneously preserve their bioactive structures, as well as obtain products of exceptional quality. This study confirms the positive effect of ultrasounds on the increase of the process efficiency and on the quantity and quality of the obtained hydrophobic fulvic acids.

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