Evaluation of the simplified method of fulvic fractions extraction from peat and lignite

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Abstract

Due to numerous and valuable properties of humic substances, preparations produced from alternative organic materials have been widely used in agriculture, bioremediations, dietary supplements and others. In addition to well-known humic acids, fulvic acids (FA) are a valuable product with a wide range of applications. The aim of performed examinations was to assess the thermal and physicochemical properties of FA obtained from lignite and peat using simplified conventional and ultrasound-assisted methods. DSC coupled with TG and MS, ^{13}C NMR, FTIR spectroscopy and differential pulse voltammetry has been used to examine extracted FA. Depending on the source of FA and the extraction method applied, their structure and properties differ. Obtained FA fractions varied for both tested raw materials in terms of analyzed carbon structures, and the highest discrepancy was observed for carbonyl groups (20.2 pp) in fractions obtained by conventional extraction. The use of the ultrasound-assisted extraction (UAE), in comparison with the traditional method, lowered the ratio of carbon in carbonyl groups by 8.4 pp and increased the ratio of aromatic and aliphatic carbon by 3.5 and 4.9 pp, respectively, for FA obtained from lignite. As for FA obtained from peat, the UAE effect appeared to be less impactful in terms of structural changes. Thermal analysis showed that the products were thermally stable up to 100 °C, and the simplified extraction resulted in the creation of mineral-organic structures that decomposed at unusually high temperatures. Simplifying the extraction process, by excluding inorganic purification and protonation of obtained FA fractions, greatly affects product quality and limits its possible application.

Keywords Fulvic acids · Organic raw materials · Thermal analysis · Extraction

Introduction

Fulvic acids (FA) are considered a fraction of broadly defined humic substances. This wide group of organic substances is defined as a heterogeneous macromolecular mixture of compounds consisting of various aromatic and aliphatic components with a complex structure and a large number of oxygen-containing functional groups. FA are classified according to the methodology of the International Humic Substances Society (IHSS) as a fraction of humic substances that are retained in moderately polar, nonionic macroporous acrylic ester resins, for example, DAX-8, at low pH [1–3]. FA play an important role in the behavior of metals and hydrophobic organic chemicals in soil and water environments [4]. Due to the variety of sources and pathways of FA generation, they have a highly complex structure, with different molecular weights, conformations, proton affinities, carboxylic, phenolic and other functional groups that bind metal cations [5].

It is believed that FA, compared to humic acids (HA), have a relatively low molecular weight, higher solubility and stronger biological activity, which is the most representative in chemical composition and function and is characterized by great application potential in various industries [6, 7]. Among the numerous industries that use humic substances (HS) in their production, agriculture determines the dynamic growth of the value of this sector. Based on an application, the agriculture segment accounted for over 50% of the revenue share in the global humic market [8]. HS are considered one of the most crucial factors in increasing crop yields,

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as they are a natural soil conditioner and act as a carbon-based chelator or microbial stimulator [9]. Although the use of HA in agriculture is more widespread, FA have also been studied for their beneficial effect on soils and crops. Researchers point to the immense potential of FA as a plant growth stimulator [10], on rice and radish [11], vegetables [12], safflower [13], coffee seedlings [14], tobacco [15] and wheat [16]. HS also have a long history of application in peloid baths, cosmetics and as components in dietary supplements and feed preparations [7]. In this case, FA play a significant role and, due to their potentially antiviral, anti-cancer, antioxidant and anti-inflammatory properties, they constitute a valuable medical substance and component of functional food.

The wide application of FA is challenged by two main factors that affect their quality and the efficiency of their obtaining process, that is, the type of raw material and the extraction method. Peat and low-quality coal (brown coal or lignite) have the greatest application potential as a standard raw material in the process of obtaining HS, including FA [17–23]. The use of low-rank carbon materials, due to their substantial resources and the pressure of European legislation on the effective use of non-renewable resources outside the energy sector, is a rational way of their management and the desired direction of development [23, 24].

A comprehensive approach to the efficient process of the production of both valuable fractions is therefore extremely important. The process of extracting HA and FA from organic materials should be properly characterized and optimized to preserve their bioactive structures and, consequently, obtain products of exceptional quality and stability.

The extraction of humic substances can be done using solutions of alkali, chelating agents, organic solvents, and aqueous salt solutions. Alkaline agents enable the extraction of up to 80% of humic acids contained in the raw material. It is advisable to use sodium or potassium hydroxides, because salts of humic substances with polyvalent cations are insoluble. Mild extraction, carried out with the use of more selective extractants, allows smaller amounts of humic substances (approx. 30% of humic acids contained in the raw material), but reduces the risk of changes in their structure under the influence of stronger chemical reagents [3]. Among the different methods, the sodium hydroxide extraction method is still popular and widely used for HS extractions in industry and laboratory [18, 25–28]. The simplicity of the method, high yield, low cost and time duration of the process is main reasons for its industrial use. Under techno-economic consideration, the production of FA and HA should be integrated if the use of additional extracting chemicals yields a significantly high quantity of FA without compromising their quality [10].

For the intensification of HS isolation, different combinations of physical, chemical or biological parameters and processes can be used. Modifications of the method by ultrasound-assisted extraction (UAE) and microwave-assisted extraction (MAE) are widely applied for the isolation of many natural products from organic raw materials, including HS [5, 29–31]. The use of modern techniques can intensify the extraction of HA and FA from potential sources, reduce the costs of this process and shorten its duration. Low-intensity ultrasonic cavitation is used as a non-thermal extraction intensification procedure. During the course of all physical operations and chemical processes, it is important to determine the influence of the process parameters on the quality of the obtained humic fractions, especially FA.

Thermal analysis has been used in the past to study various properties of organic compounds contained in natural organic matter, sediments, sludges or soils. TG–DTA or TG–DSC have been used in the past to assess and evaluate the structure stability of extracted humic fractions [32]. A complex decomposition, occurring in a wide range of temperatures, has usually been reported in the range from approximately 100 to over 600 °C. It results in the formation of carbon oxides, volatile carbohydrates and water in various quantities and proportions, depending on the atmosphere, which are considered to be products of decomposition of organic structures contained in studied HS [32–35]. Signals above 600 °C, which are typically indicative of the decomposition of carbonate minerals, are also mentioned in the literature [36]. TG–DSC coupling is considered to be a much more precise analytical method than its DTA counterpart, especially if it is further connected with an evolved gas analysis (EGA). TG studies that involved EGA have been performed a decent number of times in the form of TG–MS or TG–FTIR; however, the TG–DSC–EGA methodology tends to give the best results when it comes to the interpretation aspect due to a high complexity of the studied organic matter [37–39]. Up until now, barely any research groups used TG–DSC–EGA methodology to further evaluate studied humic fractions, while fulvic fractions, especially hydrophobic FA, remain only scarcely defined under nitrogen atmosphere [39, 40]. Studies performed in air atmosphere are going to provide more information on the thermal behavior of FA during standard storage conditions or when used in mixtures with other components, such as fertilizers.

The aim of the performed examinations was to assess thermal and physicochemical properties of FA obtained from lignite and peat using a simplified conventional (IHSS) and ultrasound-assisted methods. These two methods did not include the purification of hydrophobic FA since the contained inorganic part should not constitute ballast for use in agriculture. Inorganic substances can include sesquioxides, quartz and clay minerals, and small amounts of magnetite and crystalline minerals of silica [41–43]. Furthermore, due to the use of HF in accordance with the IHSS methodology,

this stage can pose a challenge to the process of obtaining HS on a large industrial scale.

To eliminate the influence of hydrophilic part of FA on their properties, in both methods, the practice of the IHSS was followed. FA were obtained through separation from non-humic substances in the fulvic fraction by selective adsorption onto DAX-8 resin.

Materials and methods

Collection and preparation of samples of peat and lignite

To obtain the FA, peat and lignite were used. Peat was collected from Żuławy Wiślane; Poland and lignite was obtained from Bełchatów, Poland. Once collected, both peat and lignite were dried in a laboratory dryer at 62 ± 2 °C until a constant mass was obtained and then, passed through 2.0 mm mesh sieves [2].

Methods of simplified extraction of fulvic acids

FA were obtained in two extraction processes: The first was based on a simplified version of the procedure recommended by the IHSS [44] and in the second, mechanical mixing was replaced by ultrasonic cavitation.

Both extractions started from removing polyvalent cations such as Ca^{2+} from peat (FA–P) and lignite (FA–L) using hydrochloric acid. The raw materials were acidified to pH 1–2 using 1 M HCl, and then, the ratio of 1 g of dry sample to 10 mL of 0.1 M HCl solution was obtained. The samples were shaken on a laboratory shaker for 1 h and then, separated by decantation. The residues were neutralized with 1 M NaOH. Subsequently, 0.1 M NaOH was added to acquire a sample proportion to extractant of 1:10. All extractions were performed for 4 h at room temperature under mechanical mixing (MME) or ultrasound energy influence (UAE). The power of ultrasound was set to 300 mW cm^{-2}. Suspensions formed during extractions settled overnight.

The supernatants were separated by centrifugation and acidified to pH 1 with 6 M HCl. The suspensions were left to settle for 16 h. After this time, the gel of HA was separated from the supernatant containing FA by filtration.

The FA were separated from the fraction containing dissolved FA and other organic compounds using XAD-8 resin. Adsorbed FA were removed from the resin by 0.1 M NaOH. Subsequently, the solution was concentrated in a rotary evaporator and dried in a laboratory dryer at 62 ± 2 °C until the constant mass was obtained. Samples prepared in this way were subjected to further tests.

Thermogravimetric analysis and differential scanning calorimetry coupled with mass spectrometry

Measurements were performed with the use of thermogravimetry coupled with mass spectrometry and, at some parts of the experiment, with differential scanning calorimetry (TG–MS and TG–DSC–MS). A thermal analyzer STA 449 F3 and a mass spectrometer Aëolos QMS 403 C, Netzsch, were used. The thermal program included a heating rate equal to 10 K min^{-1} to a temperature of 1450 °C or an isothermal measurement at 100 °C held for 6 h, both with synthetic air flow of 30 mL min^{-1}. Masses of approximately 10.0 mg of each sample were chosen for the experiment, with a 0.085 cm^3 alumina open crucible used. Before each measurement, an empty crucible correction to appropriate temperature was performed to compensate for thermal effects associated with properties of the crucible. All obtained results were analyzed with the use of professional software supplied by Netzsch. During mass spectrometry, the selected ion monitoring for m/z consisted of following signals: 18 (H_2O), 44 (CO_2) and 64 (SO_2).

FTIR spectroscopy

The characterization of chemical groups in FA solid samples was based on infrared absorption bands, by Fourier-transform infrared spectroscopy (FTIR), in FTIR VERTEX70 spectrometer. Samples were homogenized in a mortar with potassium bromide (KBr) and compressed into pellets. The mass ratio of sample and KBr was 1:100. The scanning was taken from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} in nitrogen atmosphere.

CP/MAS ^{13}CNMR spectroscopy

Cross-polarization magic angle spinning (CP/MAS) ^{13}C–NMR spectra for solid FA samples were made by using NMR Bruker Avance III 300 MHz. The scanning was done from -300 to 300 ppm, with probe CP–MAS 4 mm and pneumatic drive.

Differential pulse voltammetry

The manganese content in the ionic form was determined by differential pulse voltammetry (DPV) using a mercury electrode operating in the SMDE (Static Mercury Drop Electrode) mode. AUTOLAB PGSTAT 12 with GPES software and a 663 VA Stand mercury drop electrode (Metrohm, Switzerland) were used. During the test, the working electrode was a mercury electrode, the reference electrode was a silver chloride electrode, and the auxiliary electrode was a glassy carbon electrode. The measurement was carried

out from potential -1.8 to -0.5 V, with the step equal to 0.00495 V and the modulation amplitude equal to 0.00255 V. The deposition potential was -1.3 V, and the size of a drop of mercury was equal to 0.25 mm^2.

A sample of 25 cm^3 was used for the analysis. To prepare the test sample, 1.0 cm^3 of $MnSO_4$ (5 g Mn^{2+} dm^{-3}), 0.1 cm^3 of $NaClO_4$ (3 M), a sufficient volume of FA solution of 0.25 g FA dm^{-3}, so that the final concentration in the sample was 0, 10, 20, 30, 40, 50, 60, 70, 80 and 90 mg FA dm^{-3}, and demineralized water was used. The pH of the samples was adjusted to 5.0 by 0.1 M NaOH and 0.1 M HCl, and the Orion STAR A329 pH-meter was used.

Results and discussion

Characterization of fulvic acids samples

CP/MAS ^{13}C NMR results

The course of the cross-polarization magic angle spinning (CP/MAS) ^{13}C–NMR spectra for the tested FA does not indicate the destructive effect of ultrasounds. Slight differences were observed between the ^{13}C NMR spectra of the samples depending on the material they were obtained from. Those obtained from peat (FA–P) are composed of a greater number of aliphatic compounds, but also of a smaller amount of carbon corresponding to the functional groups. On the ^{13}C NMR spectra, obtained for FA–P–MME and FA–P–UAE, a similar increase in the absorption intensity can be observed in the ranges: 0–100 ppm related to the presence of carbon atoms in aliphatic connections—(Cal); 100–160 ppm as the range covering carbon atoms occurring in aromatic connections—(Car) and 160–220 ppm that indicates carbon atoms in (C–COOH) carboxyl groups. Based on the ^{13}C NMR spectra, it can be inferred that fulvic acids extracted from lignite were characterized by slightly greater structural diversity depending on extraction method than FA extracted from peat. FA–L–UAE are characterized by a more aliphatic structure with a lower content of carbon in the functional groups, but also a lower amount of carbon in the aromatic compounds than FA–L–MME. The contribution of carbon in various bonds for this fraction, calculated on the basis of defined areas under recorded peaks, presented

in Table 1, may indicate that FA–L–UAE contain less condensed structures.

However, all FA, regardless of the raw material and method of their extraction, were characterized by a significant content of desired functional groups, as all obtained FA were rich in carbonyl (ca 172 ppm) carbons.

All obtained spectra are presented in Fig. 1. The results do not show significant differences and characteristic peaks confirming differences in structure due to the extraction method. For FA obtained from peat, the share of carbon other than carbonyl is much more pronounced than for FA from lignite. In addition, a significantly higher share of aliphatic than aromatic carbon in the structure of all samples can be noticed. This is consistent with the structural characteristics of fulvic acids, which are dominated by aliphatic chains with functional groups.

Carbon signal loss in NMR spectra of HS can be attributed to the presence of paramagnetic species, unpaired electrons of which interact with nearby ^{13}C nuclear spins, diminishing or completely negating their NMR signal [45]. Although a spectrum can be obtained, the question of whether relative intensities of the resonances accurately reflect the distribution of functional groups remains. The main cause may be the presence of paramagnetic impurities [46]. It has been noted that natural organic materials may contain paramagnetic species in the form of organic free
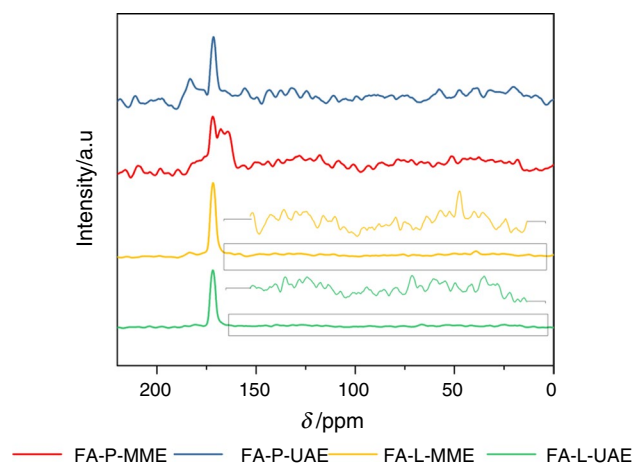

Fig. 1 CP/MAS ^{13}C NMR spectra of fulvic acids extracted from peat (FA–P) and lignite (FA–L) using two extraction types: mechanical mixing extraction and ultrasound-assisted extraction

Table 1 Relative abundances of different carbon structures measured by cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance (CP-MAS ^{13}C–NMR) in fulvic acids samples

Chemical shift/ppm	Carbon groups	Integrated area/%area			
		FA–P–MME	FA–P–UAE	FA–L–MME	FA–L–UAE
0–100	Aliphatic carbon	44.1	45.1	31.6	36.5
100–160	Aromatic carbon	27.5	26.3	19.8	23.3
160–220	Carbon in carbonyls	28.4	28.6	48.6	40.2

radicals and/or paramagnetic transition metal cations such as Fe^{3+}, Mn^{2+}, Cu^{2+} and others. Most minerals can be removed with the use of HF; however, the purification step was intentionally omitted in tested methods. HF treatment may result in the loss of carbon, as a water-soluble material, when most of the organic matter is present as organo-mineral complexes [46]. A possible explanation for this could also be that FA contain high amounts of paramagnetic sodium because sodium hydroxide is used in the HA and FA extraction, as well as during the hydrophobic FA isolation procedure.

FTIR spectroscopy results

The FTIR spectra of the FA obtained under different conditions are shown in Fig. 2. As expected, the most common bands in humic substances' FTIR spectra were present in received fulvic fractions. The spectra of standard humic substances, available on the IHSS website [2], show similarities regardless of the place of origin or the fraction tested. There always are characteristic broad peaks recorded in the area of 3800–2800 cm^{-1} and 1700–1200 cm^{-1}. This is the result of significant overlap of individual absorptions in different vibrational models by different functional groups. Obtained results are similar for both extraction methods. Only small differences can be seen between spectra of FA obtained from both raw materials, especially at the 3800–2800 cm^{-1} wavenumber ranges. The broadest and largest band is located around 3400–3000 cm^{-1}, and it is characteristic for the stretching of O–H phenols and/or alcohols and the stretching of N–H amines [47]. It is broader and more intense in
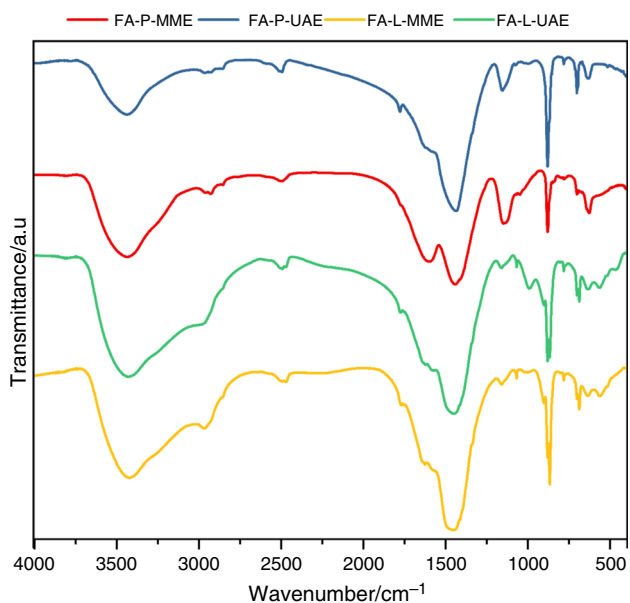

Fig. 2 FTIR spectra of fulvic acids extracted from peat (FA–P) and lignite (FA–L) using two extraction types: mechanical mixing extraction and ultrasound-assisted extraction

FA–L than in FA–P. This may point to the occurrence of these groups in greater amounts in FA from lignite.

The next band, near 2940 cm^{-1}, originated from a symmetric stretching vibration of aliphatic C–H in the CH_2 and CH_3 groups [48]. FA, especially FA–L, probably contained a long linear aliphatic chain, as indicated by main absorptions at approximately 2935 and 2860 cm^{-1}, and connected absorptions at 1470 and 720 cm^{-1} [49]. This feature is in agreement with the ^{13}C NMR data, which revealed a high percentage of aliphatic carbon in all studied samples, especially in peat, for which the band at 2860 cm^{-1} is more defined.

Isolated, weak-to-moderate intensity absorption between 2700 and 2400 cm^{-1} is usually obtained from hydride vibrations, e.g., from silanes (Si–H), thiols and sulfides (S–H), phosphines (P–H). Knowledge of the existence of the accompanying heteroatom, typical for HS, suggests that a small band around 2550 cm^{-1} can be assigned to S–H bond in thiols and sulfides. Because of the intentionally omitted purification with HF step, this band may also be assigned to Si–H bond in silanes [50].

The peak at 1715 cm^{-1} is characteristic of the C=O stretching vibration of COOH, ketones, aldehydes and esters [48] and the band at 1627 cm^{-1} to aromatic C=C stretching, amide group C=O stretching and N–H bending [47]. Some differences in the relative intensity of those bands were observed depending on the extraction method. For UAE spectra, a relatively higher absorption intensity can be observed in the free carboxyl functional group region compared to MME [51]. It may indicate that the use of UAE can influence the accessibility of those groups, although the detailed interpretation of FTIR spectra with respect to FA structural features is challenging due to overlapping effects.

One band, around 1600 cm^{-1}, with supporting bands between 850 and 670 cm^{-1}, assigned to H out-of-plane bending on an aromatic ring, and band in the region of 1150–950 cm^{-1}, assigned to the in-plane C–H bending vibrations, confirms the presence of aromatic components of FA in studied samples [49]. The main peak with the highest intensity, close to 1450 cm^{-1}, was derived from symmetric deformation of COO$^-$ and O–H and deformation of phenolic OH [52]. This feature matches results of the ^{13}C NMR data, which revealed a high percentage of carboxylic and carbonyl carbons in all studied samples. Due to use of sodium hydroxide as extracting solution, this band can also be assigned to presence of sodium from inorganic impurities [53].

Bands within the 1170–950 cm^{-1} wavenumber range can be also assigned to the C–O stretching of polysaccharides or polysaccharide-like substances and Si–O of silicate impurities [3]. Small band at wavenumber range from 785 to 540 cm^{-1} can be attributed to the C–Cl bond [50].

Obtained spectra of FA do not indicate the destructive effect of ultrasound. More significant differences can be

spotted between FA from different sources than FA obtained in two extraction types.

Thermal analysis results

Samples of four different solid FA (FA–L–MME, FA–P–MME, FA–L–UAE, FA–P–UAE) were studied with the use of TG–DSC–MS and TG–MS in order to further analyze and characterize obtained products. The thermal analysis is an important method in any quality study and could give results that allow to determine possible validity or drawbacks of used extraction processes or partially verify methodologies suggested by IHSS to study and prepare humic substances.

The isothermal program was used to assess the possibility to dry FA at 100 °C. There is no strictly determined temperature to dry FA. Lamar et al. [28] propose 90 °C, but international standard ISO 19822:2018 suggests that this procedure should be done in 65 °C [54]. The isothermal methodology was used to determine whether any mass decrease or visible heat effects occur in the sample after moisture is evaporated.

The high-temperature heating program was chosen as an additional tool to analyze thermal properties of obtained products. The standard methodology suggests that a sample should be heated up to 500 °C in order to burn all organic matter contained in it, indicating that the remainder of the residue consists of inorganic impurities [54]. All studied FA samples were heated up to 1450 °C to characterize their thermal stability and validate the suggested methodology.

Isothermal analysis

Results obtained during isothermal TG–DSC measurement at 100 °C are shown in Fig. 3. All analyzed samples exhibited an initial mass loss caused by the evaporation of physically adsorbed water that amounted to almost 9% for the FA–P–MME sample (Fig. 3c). The only atypical behavior was visible for the FA–P–UAE sample, as it started to lose mass, due to water evaporation, from the beginning of the measurement and the total mass loss was equal to 3%—which was significantly smaller than in other samples. Other than the observed difference in moisture content, all samples were characterized as stable at 100 °C, as no further mass loss or heat effect were recorded on obtained TG and DSC curves during 6 h of the isothermal program. These results suggest that the temperature of 100 °C can be considered as safe and viable for the drying process of FA, with no risk of the carbon structure degradation.
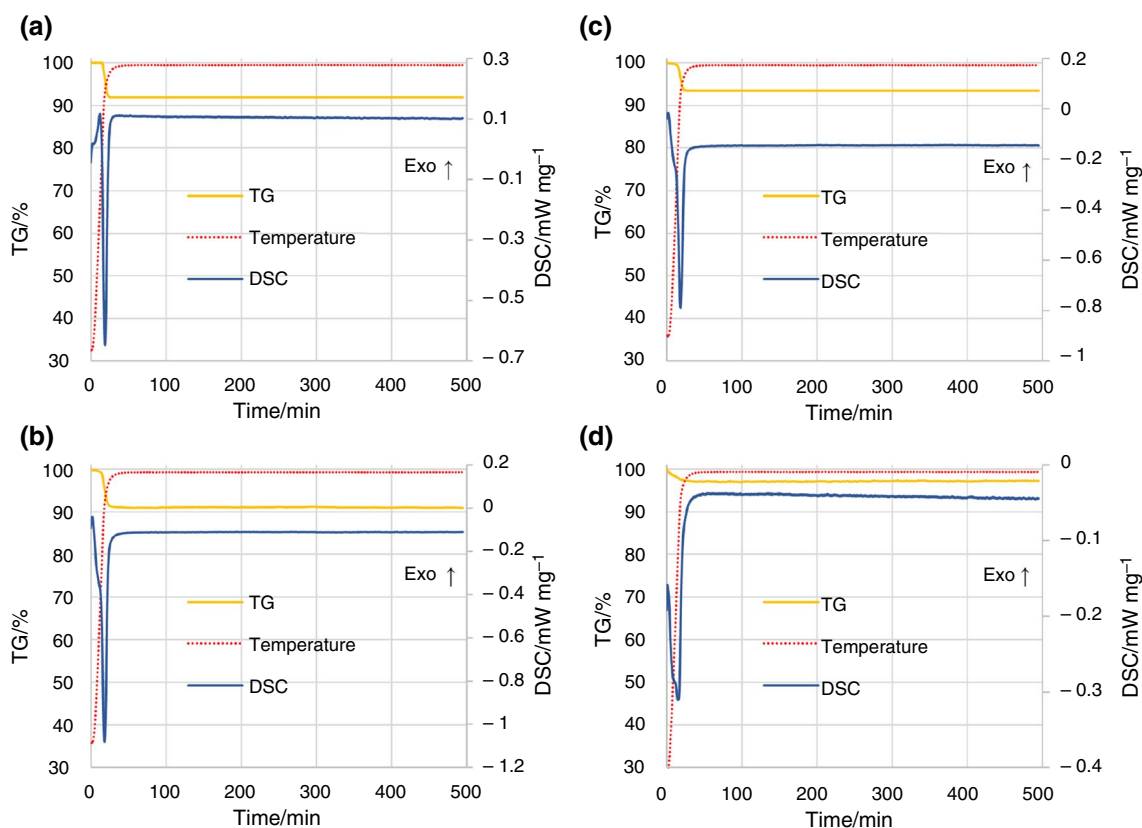

Fig. 3 TG–DSC results of the heating of studied FA samples at 100 °C for 6 h in air atmosphere. **a** FA–L–MME, **b** FA–P–MME, **c** FA–L–UAE, **d** FA–P–UAE

High-temperature analysis

Results of the high-temperature analysis of the samples are shown in Figs. 4 and 5. All tested samples were characterized by a similar path of the observed decomposition process. The general description can be used for all tested samples, with the main difference being mass loss values obtained at recorded stages of the process.

The initial part of the measurement resulted in a mass loss correlating to the one observed during the isothermal analysis. MS signals for water were visible during this stage, further proving that the moisture evaporation takes place at this stage. A small signal for carbon dioxide was also visible during water evaporation, from approximately 115 to 170 °C, indicating that a minor amount of organic carbon also decomposed. Most of the contained water was evaporated before the system reached 135 °C. The next step of the decomposition of the sample took place in the temperature range of approximately 140–620 °C. Many research groups divide the decomposition of humic and fulvic fractions into various temperature ranges, mostly fitting whole steps to obtained results and then subdividing steps into temperature ranges characteristic for assumed organic compounds [39,

40, 55]. It is suggested that the initial mass loss and the evacuation of carbon dioxide can be caused by the combustion of polysaccharides together with the decomposition of carboxyl or hydroxyl groups and simple aromatic compounds (ranging from 220 to almost 300 °C). Further mass decrease (from 300 to 400 °C) is explained by the decomposition of polar functional groups, such as carboxyl groups, or the dehydration of carboxyl functional groups in aliphatic structures. The region of the decomposition, visible above 400 °C, was attributed to the decomposition of long chain hydrocarbons, more complex aromatics, N-compounds and could also be caused by the cleavage of C–C bonds. The end of the suggested stage of the decomposition occurred with a visible, sharp effect on the $m/z = 44$ MS curve above 600 °C. It was related to a slight rapid mass decrease. All these effects may have indicated the sudden phase transition or degradation of the mineral structure, connected with the rapid release of enclosed organic compounds. The mass loss above 650 °C, which consisted of most of the decrease during the heating of studied samples, began rapidly at temperature slightly above 800 °C. No MS signal for water, a product of normal combustion process, was registered during that stage of the decomposition. The high-temperature
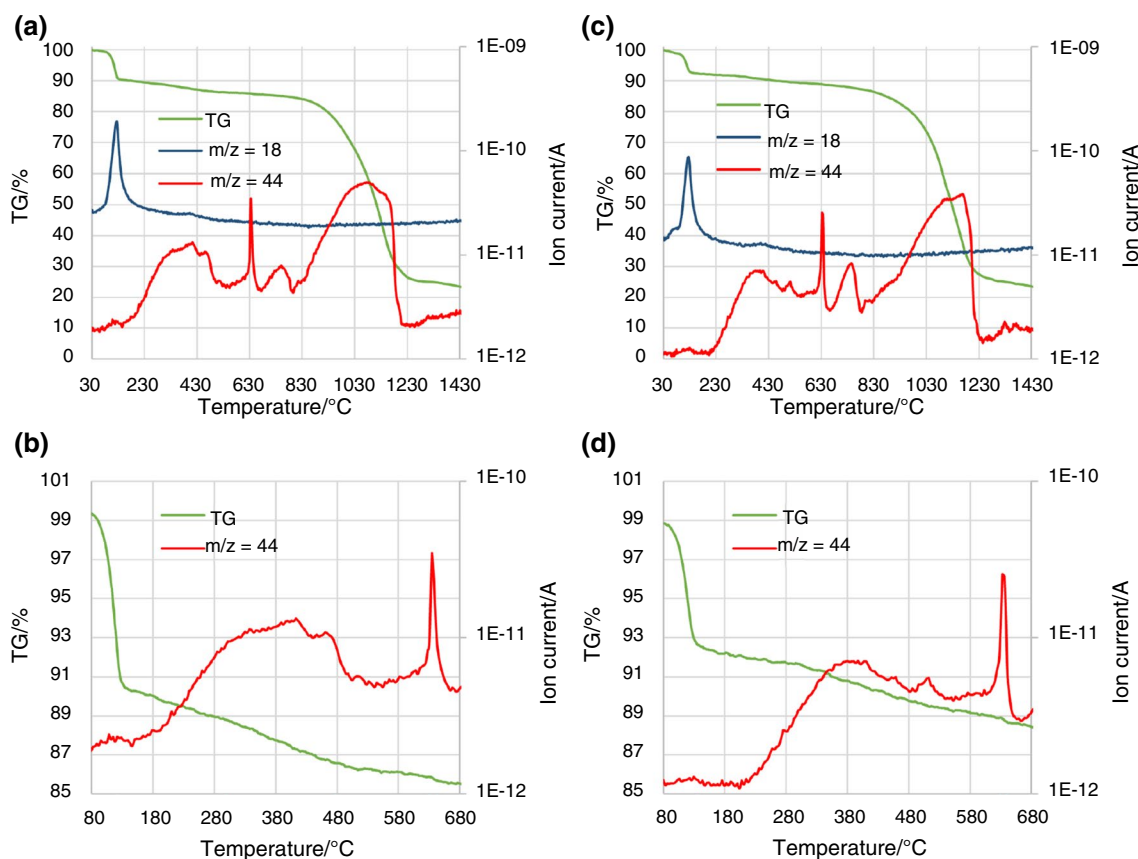

Fig. 4 TG–MS results of the heating of studied FA samples to over 1400 °C in air atmosphere. **a** FA–L–MME, **b** FA–L–MME zoom on the temperature range of the decomposition of free FA, **c** FA–L–UAE, **d** FA–L–UAE zoom on the temperature range of the decomposition of free FA
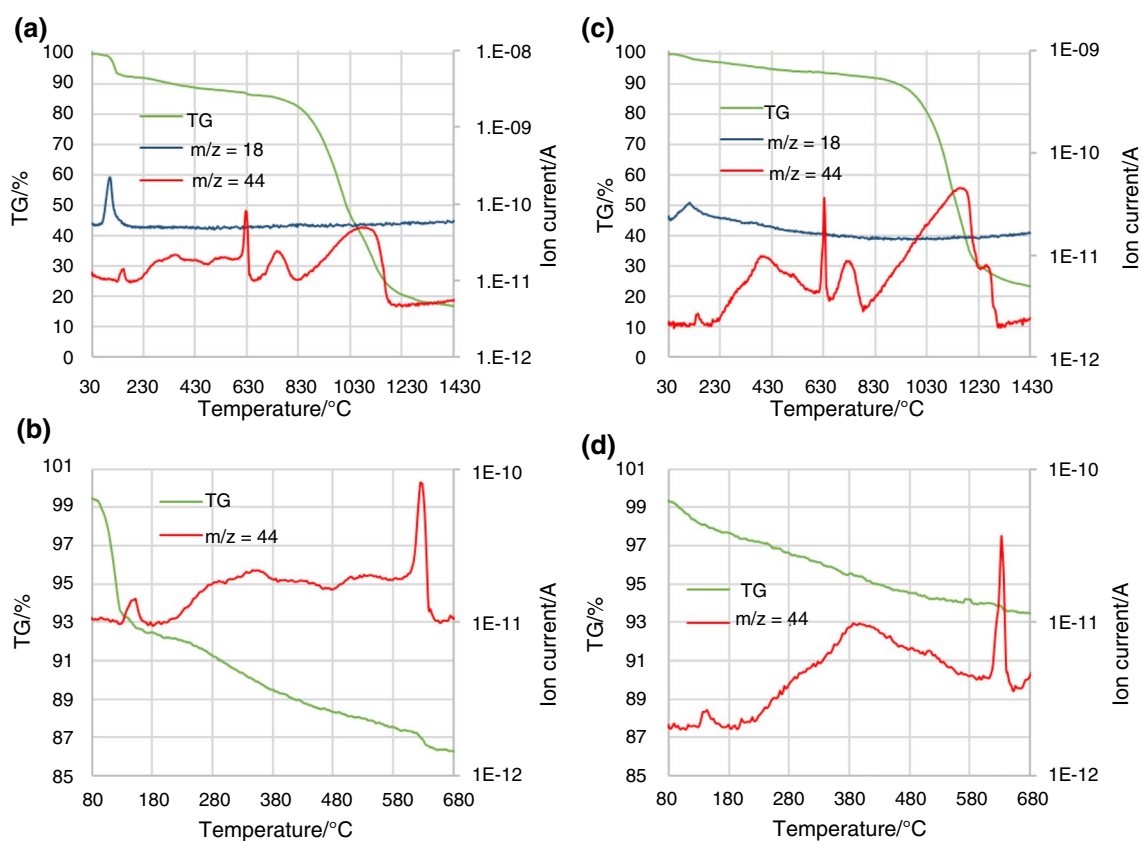
Fig. 5 TG–MS results of the heating of studied FA samples to over 1400 °C in air atmosphere. **a** FA–P–MME, **b** FA–P–MME zoom on the temperature range of the decomposition of free FA, **c** FA–P–UAE, **d** FA–P–UAE zoom on the temperature range of the decomposition of free FA

mass decrease has been noticed in studies of other research groups as well; however, there is no consistent theory on the possible cause. Some scientists suggested that the mass decrease is connected to the decomposition of the mineral part of analyzed sample, such as oxides or carbonates, which can cause a release of organic compounds that were enclosed in the mineral structure [55]. Others theorized that a phase transition of clay, from crystalline to amorphous, took place and exposed the fossilized organic carbon [56]. Due to the presence of silicates or aluminosilicates, it is also possible that a highly stable FA structure is anchored on the surface of these mineral impurities and slowly decomposes after reaching temperatures above 800 °C [57, 58]. Because of the nature of the tested extraction process, it is highly possible that obtained products contain FA salts of sodium, sodium silicates, chloride and oxide in relatively high amounts. The other possible theory could be a creation of sodium chloride with FA built into its structure, changing its thermochemical properties and causing it to melt and evaporate at lower than usual temperatures, releasing FA that were built into its structure. The lack of water generated at this stage could be explained by the prior pyrolysis of organic matter enclosed in any mineral structure that was suggested

above. Due to this phenomenon, it would be impossible to define what part of the observed mass loss of the last stage was caused by the burning of organic carbon. It is possible, however, to compare amounts of generated CO_2 during each stage of the decomposition process and assess the amount of organic matter contained in the mineral structure (bound) in comparison with the one that was registered before the temperature of 670 °C (free).

After the temperature of 1200 °C was reached by the system, a generation of carbon dioxide ended and the presence of sulfur dioxide was registered, indicating the decomposition of sulfate compounds that were contained in the studied sample.

Due to the amount of mineral impurity contained in the sample, the DSC signal has not been presented as a part of created figures, as it yielded little to no information and would only clutter generated graphs. The signal for CO_2 was measured for each experiment and compared in two distinctive ranges from 140 to 670 °C and from 670 °C to the temperature of the end of carbon dioxide generation. Each sample was characterized by the mass ratio of the free organic carbon to the organic carbon bound by mineral structures present in obtained products. Results of the carbon

Table 2 Characterization of decomposition steps of studied samples and the ratio of free and bound carbon

	Mass loss/%			Ratio/mass%	
	Dehydration	Stage 1	Stage 2	Free organic carbon	Bound organic carbon
FA–L–MME	9.63	4.83	56.42	20.1	79.9
FA–P–MME	6.74	6.87	64.11	33.9	66.1
FA–L–UAE	7.44	4.02	61.08	18.3	81.7
FA–P–UAE	2.21	4.58	64.80	18.1	81.9
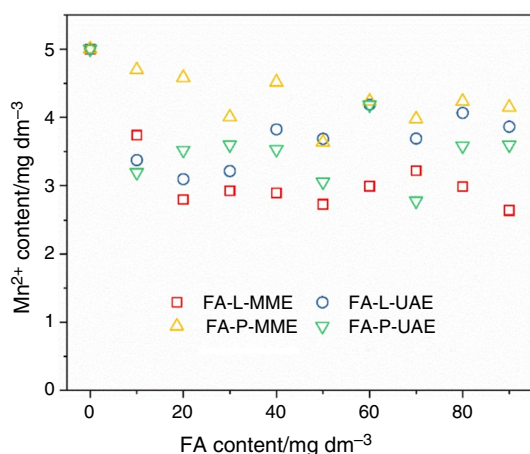
Fig. 6 Results of the DPV measurement of the Mn^{2+} cations binding capability of studied FA samples

ratio analysis, together with the mass losses of each stage, are presented in Table 2. It was determined that the extraction method had a huge impact on the composition of the peat-derived product, as the one obtained with the standard methodology contained the highest amounts of free and total organic fractions. The use of ultrasound-assisted methodology shifted the ratio of free to bound organic carbon in the FA–P sample, which could be considered as a negative effect. Thermal behavior of samples obtained from lignite was barely affected by the extraction type and the obtained product contained smaller amounts of FA in comparison with FA–P samples.

Differential pulse voltammetry

Evaluation of the ability of all studied FA solutions to bind free manganese ions was performed using differential pulse voltammetry (DPV). Results of the measurements are presented in Fig. 6. It was noted that the amount of free manganese ions bound in the solution depended minimally on the concentration of FA in the solution of the test sample.

However, after exceeding a certain critical concentration of FA in the sample, the concentration of Mn^{2+} ions stabilized. The results have presented a relationship related to the methodology used to extract fulvic acids from the coal raw material. In this case, the most significant deviations were observed when the MME was used, as the amount of Mn^{2+} ions bonded by FA was maximal at 0.85 and 2.02 mg dm^{-3} for FA obtained from peat and lignite, respectively. When UAE was used, the obtained binding profile was similar, seemingly independent of the source of obtained products. The amount of Mn^{2+} ions bound was measured up to 1.47 mg dm^{-3} and 1.32 mg dm^{-3} for peat and lignite, respectively.

The application of electrochemical analysis in the assessment of the degree of bound manganese ions by FA samples validates that the tested samples have complex properties. However, obtained results show that the DPV method for the determination of manganese ion concentration in the FA solution with inorganic impurities has significant limitations. The used method is based on the possibility of transporting ions of the analyzed metal to the electrode surface. According to Furukawa and Takahashi [59], HS, including FA, have a significant effect on the diffusion processes of metal ions present in the HS solution. Additionally, it is also important to note that FA are considered to be surfactants [60]. Quentel et al. [61] report that electrochemical analyzes can be erroneous when the amount of surfactants in the sample is significant. Additionally, solution anion strength can be disturbed because of sodium ions presence, which was the case for all samples that were obtained in this study. All above mentioned cases might be used to explain obtained results, where, as the concentration of FA in the sample increased, the measured concentration of free Mn^{2+} ions in the solution stabilized, fluctuated or even increased. This has proven that the researched simplified methodology of FA extraction does not yield products that can be characterized with binding capacities, or the methodology produces inconclusive results due to impurities or sodium salts of FA that are present in tested samples.

Conclusions

Performed research allowed to evaluate the viability of simplified extraction processes of fulvic acids and to assess the quality of obtained products.

The FA obtained from the peat had a more aliphatic structure than the lignite FA. It was also characterized with a higher ratio of aromatic carbon and a lower ratio of carbon in carbonyl groups than its lignite counterpart. The highest discrepancy was noticed for carbonyl groups in fractions obtained by conventional extraction.

The use of ultrasound-assisted extraction lowered the ratio of carbon in carbonyl groups and increased the ratio of aromatic and aliphatic carbon for the FA obtained from lignite, while for the FA obtained from peat, the effect of the UAE could have been defined as minor.

FTIR spectra indicated a presence of silicates, silanes, thiols and sulfides along with typical compounds characteristic for FA. This may have been caused by the intentional omittance of the hydrofluoric acid purification step, which is considered as the biggest inconvenience in the possible industrial scale production of FA from studied sources. Obtained spectra of FA did not indicate that the applied ultrasound methodology had any destructive effects on the structure of analyzed FA. Bigger differences were spotted between FA from different sources than FA obtained by two extraction types.

It was concluded that the drying process can be considered as safe at least up to 100 °C, without any carbon being lost from the samples. The use of isothermal, simultaneous TA allows to determine whether any unwanted transformations or degradation processes occur during the drying of the sample and should be implemented more often to validate the preparation methodology of samples that could be characterized as unstable.

Thermal analysis showed that, judging from observed mass losses, obtained products contained typical fulvic acids and organic compounds that were bound by other mineral structures present in studied systems, as the majority of observed mass loss occurred at high temperatures exceeding 800 °C. Performed analyzes confirmed the presence of high amounts of inorganic impurities that affected thermal stability of studied samples, indicating that, in the case of the simplified extraction process, some parts of the IHSS methodology, such as a suggested temperature of the dry mass verification, have to be adjusted to generate correct results. The remaining mass of every sample, up to 800 °C, is an indicator that a further purification step is a necessity if a product of high quality is to be obtained. The presence of mineral impurities can heavily influence the accessibility of extracted fulvic acids for plants, worsen certain properties and simply be considered as an unnecessary filler. Nevertheless, the sample obtained from peat with the use of standard extraction method was defined as the one that contained most free and total FA out of the studied systems.

The other conclusion could be that the proposed simplified methodology of FA extraction does not yield products that can be characterized with binding capacities, or the used DVP method generates inconclusive results due to impurities or sodium fulvic salts that are present in tested samples.

It is shown that the simplification of the extraction process, by excluding inorganic purification and protonation of obtained FA fractions, greatly affects the product quality and limits its possible applications. The excessive amount of remaining sodium should be further removed with the use of an additional ion-exchange resin column if the product is to be considered pure enough for use in the food, cosmetic, medical or pharmaceutical industries.

Declarations

Conflict of interest No conflict of interest was declared during the submission of the manuscript.

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