


Article

Peat as a Raw Material for Plant Nutrients and Humic Substances

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Abstract: The ever-increasing intensity of agriculture is causing irreversible qualitative changes in the soil. Soil conservation and improvement is a priority of EU agro-environmental policy. However, this is also one of the most difficult challenges for agriculture. Various ways for sustainable agriculture have been proposed. One way to provide arable soil with humic substances is through the use of humic extracts. The aim of this work is to create a humic product for soil improvement from local raw materials, i.e., Lithuanian peat. Lithuanian peat samples from various peatlands with a different degree of humification were studied. The chemical composition of peat was determined using various methods (chemical analysis, AAS, XRD, SEM), and the optimal conditions for obtaining peat extracts were established. After examination of the chemical composition and properties of the peat extracts produced using 0.5 N KOH, it was determined that the sample with the highest degree of humification, (H8) Ezerelio JCS “Klasmann-Deilmann” (EKD), contained: 0.7% N; 0.1% P₂O₅; 25.87% humic acids and 0.76% fulvic acids. It had a density of 1015 kg·m⁻³, dynamic viscosity of 1.490 mPa·s, electrical conductivity of 33.3 mS·cm⁻¹ and pH of 12.9.

Keywords: peat extracts; humic substances; bioresources; agriculture; chemical composition



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1. Introduction

The ever-increasing intensity of agriculture is causing irreversible qualitative changes in the soil. Soil conservation and improvement is a priority of EU agro-environmental policy. However, this is also one of the most difficult challenges for agriculture. In order to avoid the negative effect of intensive farming, the aim is to keep organic matter in the soil and to maintain properties of soil quality, such as microbiological activity, erosion resistance and soil, air and moisture regime. It is unanimously agreed upon that the use of fertilizers is essential to ensure crop yields. Various ways for sustainable agriculture have been proposed. For example, synthetic fertilizers and chemical products for plant protection are partially replaced with their biological counterparts, because fertilizers must be not only effective but also environmentally friendly [1].

Quality soil is rich in humic substances (HS), which promote the mobility of macro- and microelements and increase water retention and air permeability in the soil. With a sufficient amount of HS, the soil is solid in its structure and of a dark brown or black colour. HS have formed over hundreds or thousands of years by decomposition of organic compounds, but intensive farming is constantly reducing the amount of HS in the soil. Therefore, HS, which consist of three main groups of compounds—humic acids, fulvic acids and humins (insoluble)—are unable to regenerate [2,3]. One way to provide arable soil with HS is through the use of humic extracts [4].

Various raw materials can be used to extract HS. These include sedimentary minerals (coal, lignite, shale), peat, compost or sapropel. Originating from different sources, HS have different compositions and biological effects depending on their chemical structure and physicochemical properties [5–7]. Extracts of HS that already have industrial applications in the world are extracted from leonardites and used alone or in combination with mineral

fertilizers [8–10]. In this way, not only are the physical properties of the soil protected and improved, but the effect of inorganic fertilizers also acquires greater efficiency—the mobility and absorption of nutrients increase, and a richer yield is obtained. However, deposits of leonardites are quite limited [10,11], and the extraction of HS from coal or compost is a rather difficult and complicated process. Another possible source of HS is peat. For the most part, peat is used directly as a substrate or mixture enriched with plant nutrients. Data on the chemical processing of peat are scarce in scientific and patent literature [12,13]. There have been reports about processing technologies applying extraction methods to extract useful materials (components) from peat to be used not only in agriculture but also in medicine [14]. The interaction of sedimentary feedstock with compounds of monovalent cations (ammonium, sodium or potassium) results in solutions of HS. Alkaline extraction is one of the most popular methods for obtaining HS [15]. However, specific process conditions are highly dependent on the raw material of HS and must be adapted to the circumstances of each case.

In Lithuania, peatlands occupy about 9.9% (650 thousand ha) of the country's area; however, only about 0.2% of the area of all explored peatlands is used by the peat industry [16]. In the EU, 42% of peat is used in the crop sector, 50% in energy production, 5% to enrich the soil and 3% for other purposes. Nevertheless, in Lithuania, peat resources are mostly (90%) used for crop production and the other part (10%) as a raw material for energy production. The chemical processing of peat is not carried out in Lithuania. The use of these raw materials for the production of humic extracts would increase the use of local natural resources. Therefore, the aim of this work is to create a humic product for soil improvement from local raw materials, i.e., Lithuanian peat.

2. Materials and Methods

2.1. Materials and Sample Preparation for Analysis

In this research, chemically pure or analytical materials for extraction and chemical analysis were used. Standard methods and laboratory research equipment were used in the experiment. Methods to determine all plant nutrients (N, P, K, etc.), listed in the Fertilizer Regulation [17] or Lithuanian standards (LST), were used. Analysis was carried out using air-dried peat [18,19].

Peat samples were prepared for chemical analysis in three ways [18] and then concentrations of elements in the differently prepared extracts—the aqueous extract, the hydrochloric acid solution and the aqua regia—were determined.

2.2. Methods of Analysis

RETSCH sieves (DIN-ISO 3310/1) with a mesh size of 0.2, 0.5, 1.0, 2.0, 4.0, 5.13 and 7.0 mm [18] were used to determine particle-size distribution. The degree of humification of peat samples was determined by the von Post method [12,18,20]. The moisture content was determined by a thermogravimetric method using an electronic KERN MLS_N moisture meter with a measurement accuracy of 0.01% at a sample weight of more than 1.5 g and an operating temperature of 40–160 °C [21]. The loose bulk density and packed bulk density of peat samples were determined by the gravimetric method [21]. The density of the extracts was determined by the pycnometric method using a 5 cm³ pycnometer and electronic scales, WPS 210/C Kern ABJ (accuracy of 0.001 g). A pH meter HANNA instrument pH 211 microprocessor with a glass electrode (accuracy of 0.01) was used to determine pH (in water) and pH_{KCl} values [22]. The viscosity of the solutions was determined by the viscometer method using a glass capillary viscometer (∅ 3 mm). The refractive index was determined using a ИРФ-2 refractometer with an accuracy of 0.001 increments. The INOLAB COND 720 with an accuracy of 0.001 mS·cm⁻¹ was used to determine the electrical conductivity.

The nitrogen concentration was determined by the Kjeldahl method using a Vapodest 45s Gerhardt with an automatic titration function, using a Devarda alloy [23]. The concentration of water-soluble phosphorus (P₂O₅) and that which was soluble in inorganic

acids was determined by spectrophotometric analysis [17], using a spectrophotometer T-70+ UV-VIS with a 10.0 mm cell at the wavelength of 450 nm (accuracy ± 0.004 Abs). The potassium concentration was determined by the flame photometric method at the wavelength of 766.5 nm, using a Jenway PFP-7 flame photometer. The concentration of trace elements (Mn, Cu, Fe, Cd, Zn, Ni, Cr, Co) was determined by atomic absorption spectroscopy (AAS) using a Perkin Elmer Analyst instrument (accuracy ± 0.001 Abs). A gas mixture of acetylene ($7.5 \text{ L}\cdot\text{min}^{-1}$) and air ($10 \text{ L}\cdot\text{min}^{-1}$) was used for atomization. The carbon concentration in peat was determined by the modified Nikitin–Thurin method [24]. Samples were analysed using a T-70+ UV-VIS spectrophotometer with a 10.0 mm cell and at the wavelength of 600 nm (accuracy ± 0.004 Abs). Concentrations of humic (HA) and fulvic acids (FA) were determined using a modified method according to Dannenberg [24]. Samples were analysed using a T70+ UV-VIS spectrophotometer with 10.0 mm cells. HA was determined at the 450 nm wavelength and FA was determined at the 600 nm wavelength (accuracy ± 0.004 Abs).

Additionally, samples of peat and insoluble residue remaining after decomposition were analysed with X-ray diffraction analysis (XRD) using the Bruker X-ray AXS D8 Advance. The accuracy of X-ray diffraction analysis measurements was $2\theta = 0.01^\circ$. Operating parameters were as follows: $\text{CuK}\alpha$ radiation, Ni filter; detector movement step was 0.02° ; intensity measurement time in steps was 0.5 s; anodic voltage was 40 kV; current strength was 40 mA. SEM analysis was carried out using the scanning electron microscope PhenomWorld ProX (G5) to determine particle form and chemical composition. Magnification range: $\times 20$ –150.000; acceleration voltages: adjustable range from 4.4 to 15 kV.

2.3. Data Analysis

Depending on the repeatability, the investigation of properties of the same sample was performed 3–5 times and the arithmetic mean of the determined values is presented in this study. Statistically analytical data of micro and macro nutrient concentrations was analysed by using MS Excel data analysis (Anova, descriptive statistics) tools, calculating a range of statistical parameters for every data set. To analyse data in accordance with descriptive statistics, the observation cluster around the central location was described, and extremes are described by the degree of dispersion [25]. To evaluate results, the relative (RSD), standard (SD) and absolute (ASD) deviations were calculated at 95% probability. In all cases, the significance level was $p \leq 0.05$.

3. Results and Discussion

Only a high marsh type of Lithuanian peat was chosen to be studied. Due to its physicochemical properties, this type of peat is most often used in horticulture and gardening to improve physical and biological properties of soil. It is used to produce peat substrates enriched with fertilizers; yet, in scientific literature there is no data on the chemical processing of Lithuanian peat. Six Lithuanian peat samples from various peatlands with a different degree of humification were studied. Their properties are presented in Table 1.

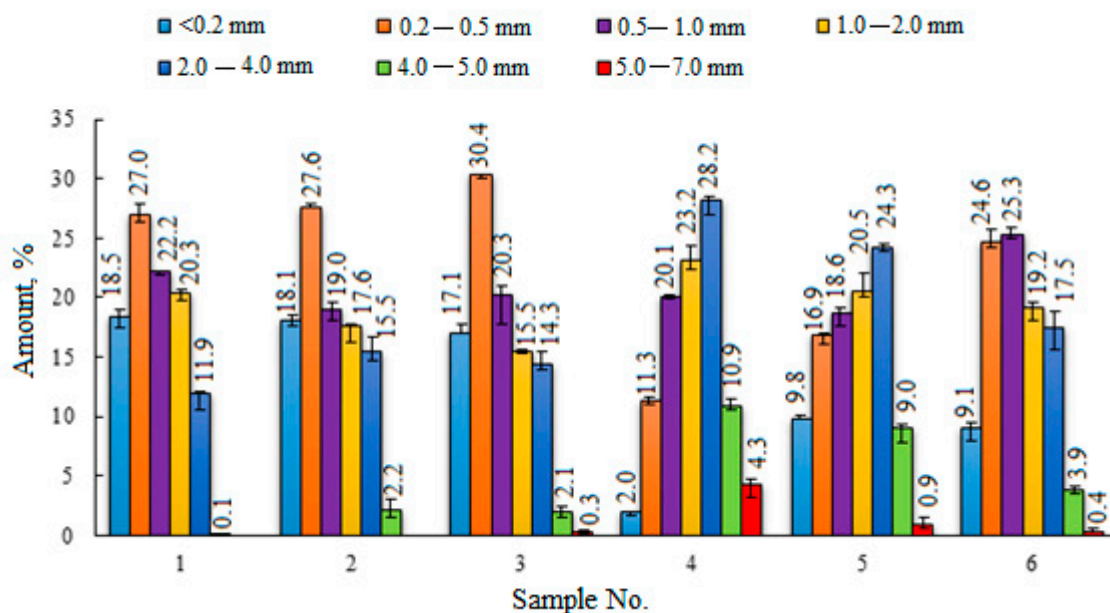
One of most important indicators when analysing the physical properties of peat is its degree of decomposition or the degree of humification. Only moderately and strongly decomposed peat (H5–H8) was chosen to be investigated in this study [12,18,20]. The pH of peat determines the solubility and availability of nutrients in the soil, and the pH value may depend on the amount of organic materials [26]. The pH and pH_{KCl} values of peat determined during the experiment showed that the pH of natural peat varies from 3.28 to 4.54, and the pH_{KCl} ranges from 2.70 to 3.66. Such pH is not conducive to the uptake of plant nutrients other than aluminium and manganese; however, excessive amounts of these elements in plants can be toxic. On the other hand, low pH indicates that organic materials in the soil have reached the stage where the released ammonia is nitrified to nitrates [27].

Table 1. Properties of peat samples.

Sample No.	Peatlands/Company	Abbreviations	pH	pH _{KCl}	Bulk Density, kg·m ⁻³		Degree of Humification (von Post Scale)
					Loose	Packaged	
1	Sepetos/JCS “Durpeta”	SD	4.15	3.66	246	409	H6
2	Didziojo Tyrulio JCS “Didysis Tyrulis”	DT	4.00	3.33	157	302	H7
3	Rekyvos SC “Rėkyva” Ezerelio JCS	RR	3.28	2.87	171	285	H6
4	“Klasmann—Deilmann” Aukštumalos pelke JCS	EKD	4.40	3.29	245	409	H8
5	“Klasmann—Deilmann” Musos tyrelio JCS	AKD	4.54	2.89	209	345	H7
6	“Laveksa”	MTL	4.45	2.70	192	295	H5

The study also assessed the bulk density of loose and packaged peat. These parameters for different samples vary in a relatively wide range: loose bulk density ranges from 157 to 246 kg·m⁻³, and packaged bulk density ranges from 285 to 409 kg·m⁻³.

The granulometric composition (%) of peat samples was determined using braided sieves of different measure ranges (Figure 1). The data show that in the first samples (No. 1–3), 20–30% of peat consists of 0.2–0.5 mm fractions. Samples No. 4 and No. 5 are dominated (about 20–25%) by particles of 2–4 mm, and sample No. 6 is dominated by particles of two sizes (0.2–0.5 mm and 0.5–1.0 mm).

**Figure 1.** The granulometric composition (%) of peat samples.

Concentrations of macro- and microelements in aqueous, hydrochloric acid and aqua regia peat extracts were determined in this study (Table 2). Different peat extracts were prepared to compare the concentration of elements found. While analysing the results of determined macro element concentrations, no significant differences were observed.

Table 2. Chemical composition of peats samples. * Insignificant.

Extract	Macronutrients Concentration, %			Microelements Concentration by Method AAS, mg·kg ⁻¹							
	N	P ₂ O ₅	K ₂ O *	Mn	Cu	Fe	Cd	Zn	Ni	Cr	Co
Sample 1 SD											
aqua	0.03 ± 0.003*	0.06 ± 0.005 *	0.01 ± 0.002	0.43 ± 0.07	0.88 ± 0.08	8.78 ± 0.55	-	4.14 ± 0.12	1.85 ± 0.11	-	0.01 ± 0.002
hydrochloric acid	1.05 ± 0.06	0.37 ± 0.005	0.05 ± 0.004	12.11 ± 0.78	24.26 ± 1.05	1749.26 ± 52.05	0.01 ± 0.002	7.09 ± 0.13	12.48 ± 0.18	0.11 ± 0.012	0.03 ± 0.002
aqua regia	-	0.39 ± 0.006	0.06 ± 0.005	14.88 ± 0.84	28.85 ± 1.55	2179.43 ± 48.09	0.14 ± 0.012	20.24 ± 0.21	18.48 ± 0.27	0.39 ± 0.022	0.04 ± 0.003
Sample 2 DT											
aqua	0.04 ± 0.004 *	0.02 ± 0.002 *	0.02 ± 0.002	0.55 ± 0.08	0.62 ± 0.06	13.89 ± 0.65	0.02 ± 0.002	6.23 ± 0.15	2.81 ± 0.16	0.01 ± 0.011	0.01 ± 0.002
hydrochloric acid	1.87 ± 0.07	0.19 ± 0.02	0.06 ± 0.006	17.21 ± 0.89	18.52 ± 0.91	2136.54 ± 44.74	0.04 ± 0.003	11.26 ± 0.12	13.79 ± 0.89	0.05 ± 0.007	0.04 ± 0.006
aqua regia	-	0.20 ± 0.02	0.07 ± 0.008	24.73 ± 1.00	19.67 ± 0.98	2630.44 ± 48.68	0.12 ± 0.012	21.16 ± 0.19	20.15 ± 0.92	0.16 ± 0.009	0.05 ± 0.007
Sample 3 RR											
aqua	0.02 ± 0.002 *	0.04 ± 0.003 *	0.02 ± 0.002	0.45 ± 0.07	0.75 ± 0.07	12.99 ± 0.85	0.04 ± 0.006	4.21 ± 0.13	2.51 ± 0.18	0.04 ± 0.006	0.03 ± 0.005
hydrochloric acid	0.7 ± 0.09	0.27 ± 0.003	0.06 ± 0.006	19.43 ± 0.91	19.87 ± 0.96	2080.95 ± 32.44	0.08 ± 0.008	10.16 ± 0.14	13.16 ± 0.14	0.16 ± 0.008	0.07 ± 0.008
aqua regia	-	0.28 ± 0.03	0.06 ± 0.005	24.81 ± 0.99	22.22 ± 1.05	2734.41 ± 35.25	0.15 ± 0.022	12.12 ± 0.25	19.74 ± 0.22	0.68 ± 0.006	0.10 ± 0.01
Sample 4 EKD											
aqua	0.05 ± 0.005 *	0.01 ± 0.002 *	0.02 ± 0.002	0.35 ± 0.05	1.59 ± 0.12	19.70 ± 0.87	0.01 ± 0.002	4.15 ± 0.12	3.60 ± 0.19	0.08 ± 0.004	0.04 ± 0.003
hydrochloric acid	2.11 ± 0.21	0.11 ± 0.01	0.06 ± 0.006	16.08 ± 0.88	33.5 ± 1.21	3120.91 ± 35.59	0.03 ± 0.004	12.40 ± 0.14	21.50 ± 0.98	0.95 ± 0.006	0.61 ± 0.055
aqua regia	-	0.14 ± 0.01	0.07 ± 0.006	21.33 ± 0.97	35.7 ± 1.28	3918.26 ± 32.28	0.12 ± 0.02	18.03 ± 0.13	23.2 ± 1.01	1.12 ± 0.016	0.82 ± 0.085
Sample 5 AKD											
aqua	0.04 ± 0.004 *	0.02 ± 0.002 *	0.01 ± 0.002	0.31 ± 0.04	1.07 ± 0.11	11.26 ± 0.65	0.08 ± 0.009	8.44 ± 0.13	2.30 ± 0.22	0.06 ± 0.004	0.05 ± 0.005
hydrochloric acid	1.43 ± 0.11	0.17 ± 0.02	0.05 ± 0.004	13.00 ± 0.81	20.11 ± 0.98	1972.63 ± 20.48	0.12 ± 0.02	12.88 ± 0.17	9.60 ± 0.52	0.46 ± 0.005	0.48 ± 0.056
aqua regia	-	0.20 ± 0.02	0.06 ± 0.006	21.49 ± 0.98	27.16 ± 0.97	2630.47 ± 28.00	0.17 ± 0.02	24.89 ± 0.92	13.79 ± 0.72	0.53 ± 0.065	0.72 ± 0.075
Sample 6 MTL											
aqua	0.03 *	0.07 ± 0.005 *	0.01 ± 0.002	0.42 ± 0.06	1.41 ± 0.14	9.76 ± 0.55	0.07 ± 0.009	5.61 ± 0.12	2.20	0.06 ± 0.005	0.02 ± 0.003
hydrochloric acid	1.28 ± 0.11	0.41 ± 0.05	0.05 ± 0.006	20.17 ± 0.93	28.54 ± 1.06	1804.62 ± 25.20	0.12 ± 0.01	7.65 ± 0.18	7.86	0.48 ± 0.051	0.35 ± 0.042
aqua regia	-	0.42 ± 0.06	0.06 ± 0.008	26.38 ± 1.01	30.14 ± 1.02	2274.58 ± 22.87	0.14 ± 0.02	8.69 ± 0.17	14.28	0.69 ± 0.058	0.83 ± 0.086

Slightly higher nutrient concentrations were found in the hydrochloric acid and aqua regia extracts, and this is related to the solubility of the compounds present in the samples. However, in this case, decomposition with aqua regia is not informative because nitrogen concentration cannot be determined.

Nitrogen concentration in peat is an important agrochemical qualitative indicator. According to various authors [27,28], nitrogen concentration in peat varies from 0.7% to 4%. The values of nitrogen concentrations determined in aqueous extracts are very low and of low statistical reliability. Therefore, it can be stated that water-soluble nitrogen has not been found in peat. Nitrogen found in organic compounds in peat was mineralized by decomposing the samples with mineral acids, and this was the reason why its concentration in the samples was higher. The highest nitrogen concentration (2.11%) was found in the EKD (sample 4), and a significant amount of nitrogen was found in samples 2 and 5 (1.87% and 1.43%, respectively). The lowest concentration of nitrogen (0.7%) was determined in the RR sample (sample 3). The concentration of phosphorus found in peat is especially low—it accounts for up to 0.42%. Most of the phosphorus is in organic compounds, so the concentration of phosphorus available to plants (water-soluble) is very low. After the samples were decomposed with mineral acids, higher ($p < 0.05$) phosphorus concentrations (0.11–0.42%) were determined. These results of our research coincide with the trend found in works of other authors [27,28]. Analysing aqua regia extract data, it was observed that higher amounts ($p < 0.05$) of phosphorus are present in the samples with lower humification: for example, in H5, there is 0.42% P_2O_5 (MTL, sample 6), while H8 includes only 0.14% P_2O_5 (sample 4 EKD). This regularity, i.e., a negative correlation between phosphorus and humification, has been noticed and described by other scientists in their work [29]. In all cases, the potassium concentration in peat extract samples is even lower and insignificant.

Continuing the research, the concentrations of the trace elements Mn, Cu, Fe, Cd, Zn, Cr and Co were determined by the AAS method. To determine macronutrients, this study used extracts of water, hydrochloric acid, and aqua regia. Analysing the results of trace element concentration, differences in concentration values are observed, which are highly dependent on the method of sample preparation. Aqueous extracts have the highest Fe concentration (8.8–19.7 $mg \cdot kg^{-1}$), as well as Zn, ranging from 4.14 $mg \cdot kg^{-1}$ (SD) to 8.44 $mg \cdot kg^{-1}$ (AKD). Concentrations of other trace elements are even lower and fluctuate across a wide range, from 0.01 $mg \cdot kg^{-1}$ to 6 $mg \cdot kg^{-1}$.

Decomposition with acids showed much higher concentrations of trace elements. The highest content of iron was found in the extracts of hydrochloric acid and aqua regia. In the HCl extract, the highest iron ($p < 0.05$) content was found in EKD peat samples (sample 4). Here, the iron concentration was found to be 3120.9 $mg \cdot kg^{-1}$. Accordingly, a higher concentration of iron (3918.26 $mg \cdot kg^{-1}$) was found in the aqua regia extract of the same sample. Small amounts of other trace elements compared to iron concentration were detected in both acid extracts. Data in the literature confirm experimentally obtained results that peat contains high concentrations of Fe, and the concentrations of other trace elements vary across a wide range [19,30,31].

The carbon concentration in peat was determined by the spectrophotometric, modified Nikitin–Thurin method. The obtained results are shown in Figure 2.

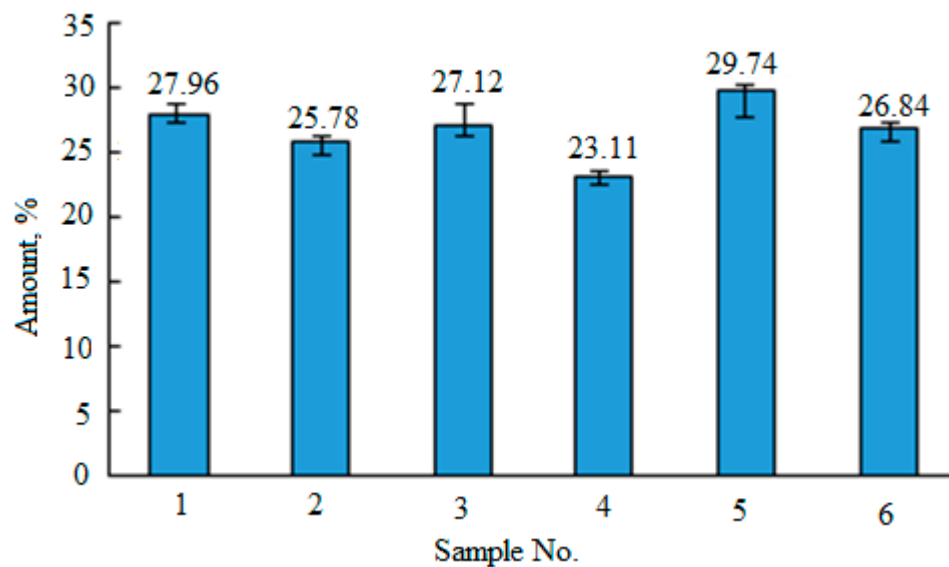


Figure 2. Carbon concentration in peat samples.

The carbon concentration in peat varies from 23.0% to 30.0%. According to the scientific literature, peat with higher carbon concentration should be chosen for the extraction of humic acids. This recommendation is explained by the fact that the higher carbon concentration, the higher amount of humic acid extracted [15].

Many scientific papers and reviews indicate that peat is a multisystem, composed of an organic and a mineral part. To determine the composition of the mineral part, X-ray diffraction analysis (Figure 3) of peat samples was performed. The data obtained in the research confirm the data available in scientific literature.

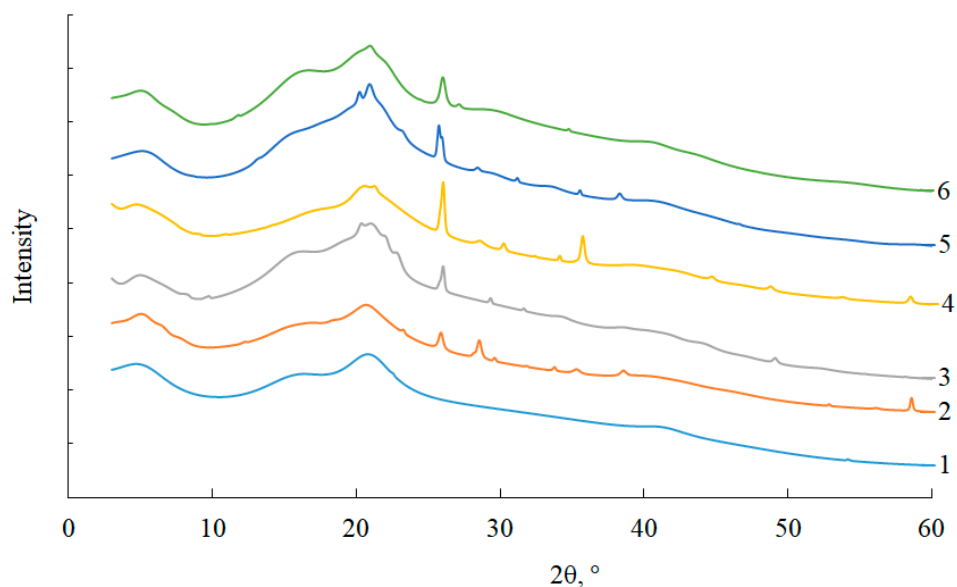


Figure 3. XRD of peat samples.

Comparing the data of X-ray analysis of peat from different peatlands (Figure 3), it is obvious that the nature of XRD curves of all analysed peat samples is analogous and characteristic to amorphous matter. The XRD curves show a characteristic hump between 18 and 35° [32]. Several low-intensity peaks are characteristic to SiO₂, the only crystalline component in the samples. Only the intensity of the peaks and the number of

peaks themselves differ slightly. Peat X-ray curves, obtained during the research, coincide to a great extent with the XRD curves of amorphous cellulose, as described by other researchers [32,33]. The results of the analysis show that the amounts of mineral impurities (sand and clay) detected in the main part of the amorphous samples are very small and vary over a wide range. The most important factors resulting in impurities are formation (degree of decomposition) and peat mining conditions [33].

The results of the chemical composition analysis are supplemented with the data obtained from the SEM analysis. Figure 4a,b presents the results of the SEM analysis of an EKD peat sample.

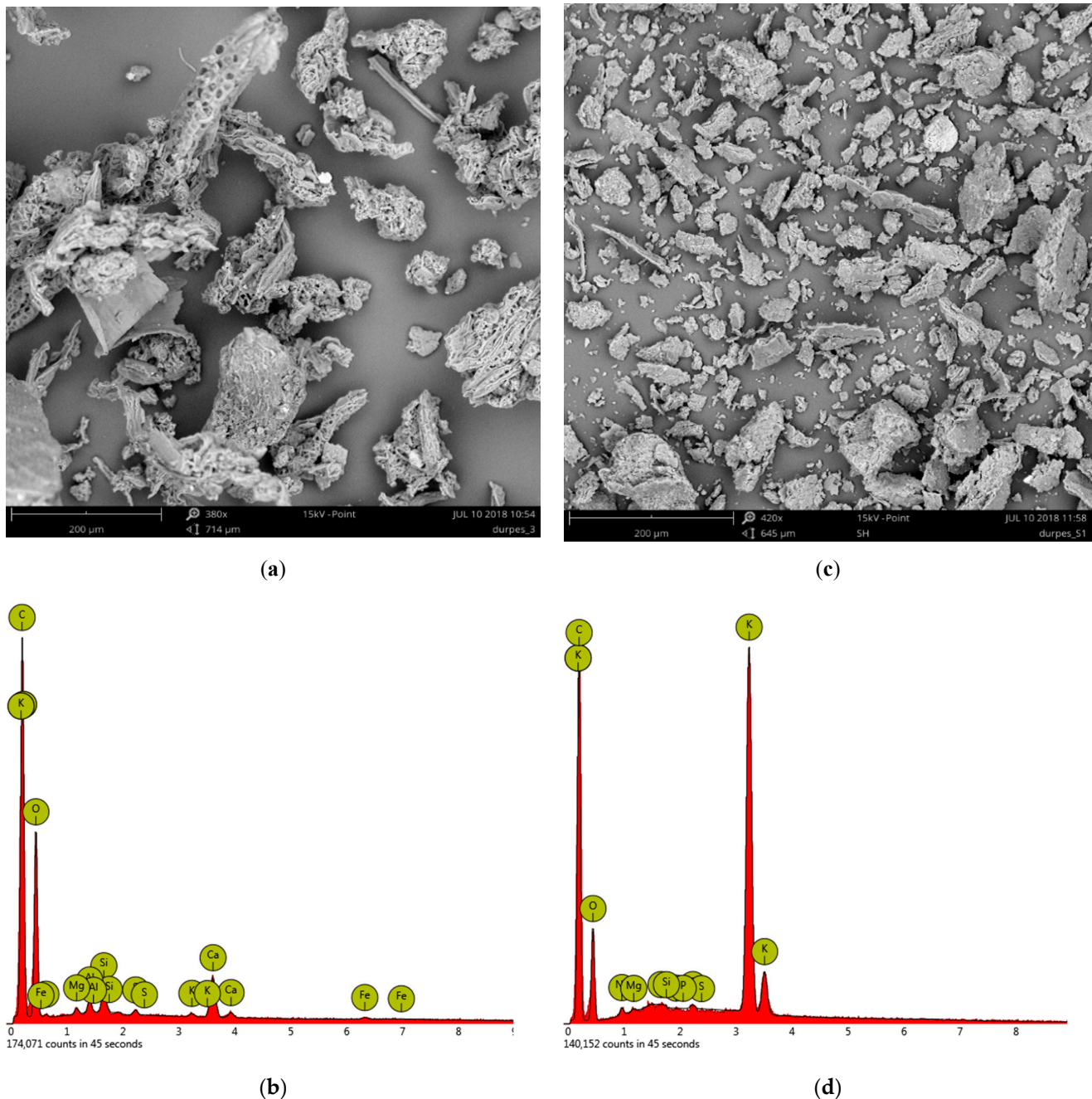


Figure 4. SEM results of peat samples before (a,b) and after (c,d) extraction.

The unevenness of the chemical composition of peat could be explained by the fact that it contains organic and mineral parts and high moisture content. Peat contains particles

of various shapes and sizes; therefore, many researchers classify it as a polydisperse and polyfractional system. Depending on the conditions, the components of the peat system may exist not only in different compounds but also in different states of both true and colloidal solutions. Differences obtained in the analytical results could be explained by the individual composition and structural features of the composition of peat, which depend on the botanical composition, the degree of humification, the formation and the environmental conditions. In summary, it can be stated that the results of samples from different peatlands, when compared to each other, differ, and this is also described in studies of other researchers [15,19,27–29].

Humic acids are obtained during an extraction process based on the solubility of HS at different pH values of the solvent. HS include humins, humic acids and fulvic acids. These compounds are usually extracted from Leonardites, other rocks or compost. As humins are insoluble in neither acids nor alkalis, these substances precipitate in the sediment together with inorganic compounds. Humic acids do not dissolve when the pH of the solvent is less than 7, and fulvic acids dissolve at any pH. It is for this reason that humic acids are extracted using an alkaline solvent. Several extraction solvents for humic and fulvic acids have been identified in scientific literature. These include sodium hydroxide, sodium pyrophosphate and potassium hydroxide [4,15]. In comparison, KOH extracts more humic acid from peat than NaOH [15]. Although the use of NaOH is more economical, the use of KOH supplies the soil and plants with an additional macroelement, potassium. Therefore, KOH, as the most effective solvent, was chosen to be studied.

The study used less than 0.2 mm fraction of peat from different peatlands; 0.1 N, 0.25 N and 0.5 N concentrations of potassium hydroxide solution; and a ratio of peat:extractant equal to 1:20. The extracts were produced by continuous shaking with an electric shaker. When this ratio and the smallest fraction of peat are used, the peat is completely submerged and does not absorb all the extractant. During the study, the dependence of the refractive index on the interaction durations in the room temperature was followed (Figure 5).

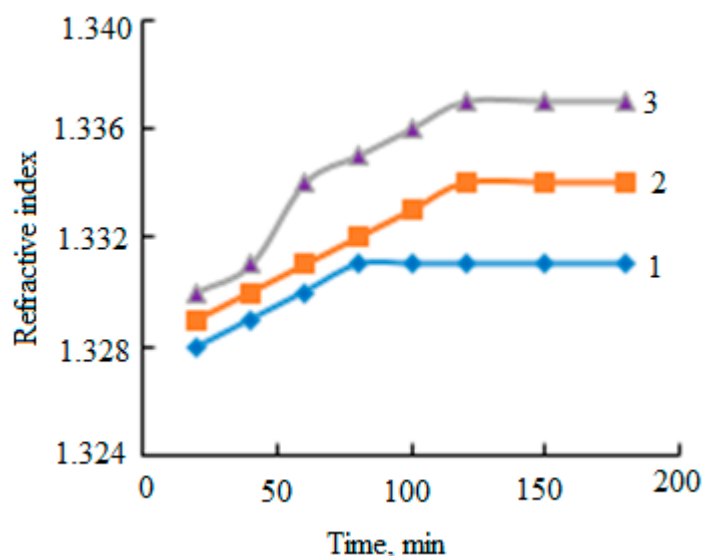


Figure 5. Dependence of refractive index on interaction durations of different concentrations of KOH solution: 1–0.1 N; 2–0.25 N; 3–0.5 N.

In the study, it was observed that the refractive index stabilizes faster when using 0.1 N alkali for extraction, but higher refractive index values are achieved when solutions of higher concentration are used. Higher refractive index values usually indicate that the solution contains higher amounts of macromolecules, as humic and fulvic acids are known to consist of large macromolecular compounds [34]. Thus, it can be concluded that with an increasing value of the refractive index, the extract contains more dissolved humic

acid. Figure 5 shows the dependence of the refractive index of EKD peat extract on the extraction time. It can be seen that the extraction is fairly even, and the slight scattering of the experimental results may have occurred due to unevenness in the organic composition of the peat.

Density, viscosity, pH and electrical conductivity values were determined at certain time intervals (80, 160 and 240 min) to select the duration of the extraction process. Time intervals were chosen according to what was described in scientific literature, when the recommended extraction time did not exceed 240 min. It is stated that the oxidation of humic acids may occur if the interaction period is too long [4,15]. Analysis of obtained data showed that the values of the extract density and viscosity increase with increasing duration of extraction. Values of electrical conductivity and pH did not change during the experiment and depended only on the concentration of KOH used.

After evaluation of experimental data and in order to obtain the highest possible amount of humic acids and to develop an economical production technology, it was decided to use a KOH solution with the maximum concentration of 0.5 N. It is also possible that the use of a higher concentration of potassium hydroxide solution would increase the pH of the extract even more. Strongly alkaline extract can affect the properties of fertilizers and at the same time have an adverse effect on plants and soil.

The optimal conditions for obtaining peat extracts have been determined. They are as follows: peat fraction is <0.2 mm; peat–extractant ratio is 1:20; extractant is 0.5 N KOH; and extraction time is 2 h, when the extractant is constantly stirred. The extracts prepared under these conditions were filtered off; the precipitate was dried and weighed. The precipitate and extracts were analysed and the obtained results (all values satisfy the condition $p < 0.05$) are shown in Table 3.

Table 3. Properties of peat extracts.

Sample	pH	Refractive Index	Electrical Conductivity, mS·cm ⁻¹	Density, kg·m ⁻³	Viscosity		Humic Acids, %	Fulvic Acids, %	Sediment Content, %
					Kinematic, mm ² ·s ⁻¹	Dynamic, mPa·s			
1	13.05	1.337 ± 0.001	40.2	1016	1.452	1.475	14.38 ± 0.11	0.31 ± 0.05	79.57
2	13.12	1.338 ± 0.001	46.7	1016	1.393	1.415	16.56 ± 0.15	0.32 ± 0.07	86.83
3	12.91	1.338 ± 0.001	40.1	1016	1.367	1.389	12.32 ± 0.10	0.22 ± 0.08	81.25
4	12.94	1.337 ± 0.001	33.3	1015	1.468	1.490	25.87 ± 0.19	0.76 ± 0.14	66.99
5	13.01	1.337 ± 0.001	42.1	1018	1.421	1.447	15.31 ± 0.37	0.60 ± 0.17	81.65
6	13.04	1.338 ± 0.001	47.8	1017	1.407	1.431	13.18 ± 0.14	0.55 ± 0.19	88.23

The values of the physical parameters of the extracts prepared under optimal conditions were similar: the pH value varied around 13; refractive index varied around 1.338; density varied around 1016 kg·m⁻³. The minimum value of kinematic viscosity measured was 1.367 mm²·s⁻¹ and the maximum was 1.468 mm²·s⁻¹. Values of electrical conductivity differed slightly more than other physical parameters, i.e., from 33.3 mS·cm⁻¹ to 47.8 mS·cm⁻¹. This may have been due to the concentration of macro- and microelements and humic acids in the peat from different peatlands. These properties could be suitable indicators enabling the control of the extraction process.

The highest humic acid concentration of 25.87% was found in the peat extract of EKD (sample 4), and the lowest of 12.32% in the peat extract of RR (sample 3). The concentration of fulvic acids in all samples did not reach 1%, but the highest concentration of these acids was found in the peat extract from EKD (sample 4) peatland (0.76%).

Due to the fact that during the extraction, humic acids pass into the soluble phase and the humins remains in the solid phase, the weight of the precipitate after extraction was determined. The least sediment (about 66%) remained after alkali extraction in the EKD sample, which has the highest degree of humification H8. SEM analysis of the sediment was performed (Figure 4c,d), the results of which show that after extraction peat particles decrease, and their chemical composition changes.

Waste generated after the extraction of HS can be used for the preparation of growth media or substrates. They do not contain any harmful substances, and there is a possibility to enrich the mixtures. This would already be a separate field of research for the development of a complex waste-free recycling technology.

After that, the concentration of macronutrients (N and P_2O_5) in the extracts was determined (Figure 6). As 0.5 N KOH was chosen as the extractant, the content of the macronutrient potassium was not determined.

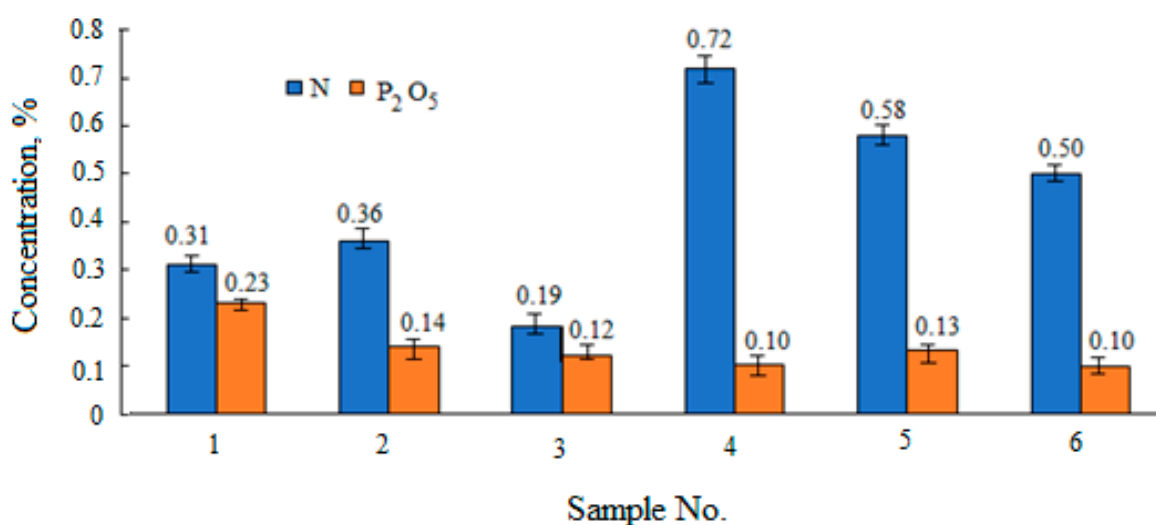


Figure 6. Concentration of macronutrients (N and P_2O_5) in the extracts.

The data in Figure 6 show that the concentrations of macronutrients N and P_2O_5 in potassium hydroxide solutions are different because they depend on the peat and the degree of humification. The obtained data correlate with the results of chemical analysis of raw peat (Table 2).

4. Conclusions

Lithuanian peat samples from various peatlands with a different degree of humification were studied. After investigating the chemical composition of peat in different Lithuanian peatlands, it was determined that peat with the highest degree of humification H8 (EKD sample) has the highest concentration of nitrogen and potassium but the lowest phosphorus concentration. Different concentrations of trace elements (Mn, Cu, Fe, Zn, Co, Ni and Cr) were found in all peat samples. Peat extraction conditions were experimentally investigated, and it was found that the optimal peat fraction is less than 0.2 mm; the ratio of peat to extractant is 1:20; the extractant is 0.5 N KOH and the duration of the extraction process is 2 h. Extracts prepared under these conditions are stable at room temperature and can be stored safely for a long time (2–3 months). After examination of the chemical composition and properties of the peat extracts, it was determined that the prepared peat extract can be used as a source of humic substances in fertilizers.

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