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Evaluation of the possibilities of using humic acids obtained from lignite in modern water treatment

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ABSTRACT

The aim of this study was to evaluate the possibilities of using humic acids obtained from lignite in modern water treatment. The humic acids (HAs) were extracted from polish deposit of lignite – Sieniawa Lubuska by alkaline extraction using for this purpose following extractants: 0.1 M NaOH – HAs SN0.1 and 0.1 M $Na_4P_2O_7$ – HAs SP0.1. In order to assess the impact of extractant on the sorption properties of the examined humic acids, their specific surface area and the content of active functional groups were determined. Thermo-oxidative behavior of examined humic substances was investigated employing the thermal analysis. The humic acids obtained from lignite were characterized also by ^{13}C NMR spectroscopy. In addition to demonstrate the potential of examined humic acids as a low-cost reactive barrier material for environmental protection applications of toxic metals, sorption of Cr(VI) on the HAs was carried out using a batch method. The structure of obtained humic acids was undoubtedly influenced by the type of extractants used for their isolation. In structure of humic acids derived from lignite the aliphatic connections were dominated. Their participation in HAs obtained by using 0.1 M NaOH amounts to 78.9% and 58.5% for sample obtained using 0.1 M $Na_4P_2O_7$. The highest content of all acidic functional groups - referred to total acidity (TA) is characterized by HAs obtained by extraction with 0.1 M $Na_4P_2O_7$ and it was 7.69 mmol/g. In lignite humic acids the carboxylic groups, assigned to peak in the range of 160–190 ppm of ^{13}C NMR spectra constituted for HAs SP0.1 – 3.54% and 2.40% for HAs SN0.1. The specific surface area for all humic acids samples was high from 370.0 to 394.4 m^2/g and correlate with the results of humic acids acidity. The sorption of Cr(VI) on the surface of HAs depends strongly on the pH and Cr(VI) sorption increased with a decreasing pH. It was observed that the removal efficiency of Cr(VI) was the highest for SP0.1 and decreased from 79.8% to 66.5% with the rise of pH from 2 to 5. Therefore and because of the highly developed specific surface area of examined humic acids as well as the presence of hydrophilic functional groups resulting in their specific sorption and ion exchange properties can be an attractive and inexpensive option in the water treatment.

Keywords: Humic acids; Water treatment; Lignite; Extraction

1. Introduction

Heavy metal and organic contamination of surface and groundwater are a major environmental concern. The contamination is due to their occurrence in the natural environment as well as from human activity, and more specifically from industrial processes. The contamination removal techniques most commonly used in industry include the following techniques: precipitation, adsorption and biosorption, coagulation, solvent extraction and ion exchange and as well as membrane processes [1,2]. Each process shows advantages

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and disadvantages. There is not only one typical technologies for treatment of contaminated water. Many waters are contaminated with mixed wastes, which conventionally first are treated with one method to remediate only one class of contaminants and then second method to remove another type of contaminants. Because different methods operate on different principles, both technologies are applied sequentially, rather than simultaneously. This conventional two-step approach to water treatment is very expensive and disadvantageous to use. A novel material having properties to remove both classes of contaminants in one step is a perspective direction in the development of modern water treatment. Using humic acids obtained from lignite as sorbents in water treatment now offer an attractive and inexpensive option for the removal of colloidal and dissolved metals and the aim of the manuscript was to demonstrate the potential of HAs in comparison with, for example, activated carbon.

The versatility of activated carbon makes it an effective option for gas phase, drinking water and wastewater treatment. There are many different varieties of commercial activated carbons for various water treatment applications that can have affinities to different substances [3,4]. In many conventional water treatment plants mainly microporous activated carbons, which are efficient for removal of organic compounds with small sizes are used [5]. A highly porous carbon structure is formed from, for example, bituminous coals, wood, coconut shells by heating in the absence of air, then activation of the carbonized material by additional heating under oxidizing conditions. Activated carbons can be produced also with chemical activation by impregnating the raw material with chemical substances and then heating to lower temperatures [6–8]. The high cost of obtaining activated carbon leads to the search for cheaper substitute or where possible waste as adsorbents for treatment of contaminated water [4,7,9].

The specific sorption and ion exchange properties of carbonaceous materials are related to the amount and structure of humus substances contained within it. The chemical structure of these compounds and the contents of reactive functional groups enable mineral–organic linkages of a different kind to be obtained. Cation–humic interactions exert a control over the reactivity of the cations, including its bioavailability. The character of these linkages has an influence on the mobility of metal ions in the environment. Organic ligands, which humic substances are, constitute particularly valuable elements on account of environmental protection, due to their ability to bind the pesticides. They can also immobilize and neutralize the environmental negative effect of heavy metals by removing these toxic ions, contributing to the process of detoxification [10–12].

Humic substances are a group of distinctive organic compounds such as humic acids (HAs), fulvic acids (FAs) and humins, which are created in complicated biochemical processes, such as oxidation, condensation and polymerization of high-molecular products of plant and animal residue decomposition. The most interesting, in application point of view, are humic acids [11].

Humic acids are complex molecules built of aromatic core containing phenol or nitrogen in cyclic form. The core binds with sugars, peptides, amino acids, acids and other aliphatic compounds [13,14]. From a chemical point of view, humic substances can be described generally as a concentration of aromatic and aliphatic rings, aliphatic chains, bridges and numerous functional groups. Among the most important functional groups of humus compounds are carboxyl, hydroxyl, phenolic, methoxyl and carbonyl groups. Their presence, a negative charge exactly being formed on them allow for the formation of the linkages of humic substances with metal cations. The major binding sites are attributed to the oxygen-containing functional groups – carboxylic and phenolic groups, which contribute to the TA of humic substances [15–17].

The chemical and physical characteristics of humic acids, which have not been precisely defined, are strongly dependent on the source they originate. They are commonly found in soil, waters and rivers. Humic acids are also a component of peat, coal (especially lignite) or leonardite [18,19]. In Poland due to economic and technological developments, it seems real to use lignite as a material for obtaining humic acids. This is important for the regions close to opencast mines producing lignites. Detailed characteristics of some lignites from different coal basins in Central and Eastern Europe, including the yields and elemental analyses of lignite humic acids have been published elsewhere [20,21]. Poland is currently the second lignite producer in the European Union as well as the seventh in the world. Generally, the lignite-bearing areas cover about one-third of the Poland's total territory [20,22,23] and is concentrated in five regions of central and western Poland [24]. Lignite production in Poland reached up to 62.9 Mt in 2011 [25]. These lignite seams are of Early and Middle Miocene age and among the genetically most differentiated in the world. Lignite in the dominant degree is used for energy purposes, however in the age of rational utilization of non-renewable resources, technological progress leads to the focus on lignite utilization outside the energy sector such as agriculture or environmental technologies. Application of them as a rich source of humic acids is also a rational way of managing them. The yields and propriety of humic acids depend on source of origin as well as method of their extraction.

Humic acids have many applications, among others, as dyes, wood hardening agents and they are also used in veterinary medicine or synthetic polymers production [26]. However, they are used most commonly in agriculture, because of their colloidal character and huge active surface giving them fine adsorptive properties [27]. In natural environment, humic acids form proper structure of soil, facilitating water retention, improving porosity and consequently aeration. Sorption and ion exchange properties also allow to supply necessary micro- and macronutrients to plants and eliminating from the ground ionic and molecular impurities in the form of heavy metals [27–30].

The highly developed specific surface area of humic acids and the presence of hydrophilic functional groups resulting in their specific sorption and ion exchange properties are also required in the purification of water. One of the preparations available on the market used for this purpose is HUMASORB-CS^{TM}. HUMASORB-CS^{TM} manufactured by Arctech Inc., which is a lignite-derived ion exchange sorbent for removal of metals and organic contaminants from groundwater and surface water streams in one processing step. It is a proprietary polymer based upon the organic structure of humic acids and consists of a mixture of molecular units [31,32].

Chemical and physical properties of humic substances obtained from polish lignite as a component in the production of commercial preparations should be characterized by similar features. One of the basic factors affecting the useful properties of humic acids is the way of processing raw materials in the production process. The process of obtaining humic acids from organic materials should be characterized by parameters in order to preserve their bioactive structures and consequently obtain products of exceptional quality

The aim of present examinations was the assessment of physicochemical properties of humic acids obtained from lignite using 0.1 M NaOH and 0.1 M $Na_4P_2O_7$, the most popular reagents used for extraction of organic constituents from soil. The humic acids used in the present work were obtained from polish deposit of lignite – Sieniawa Lubuska. The results were compared with the results of analyzes for technical humic acids (KHtech) – the commercial humic acids purchased from Sigma-Aldrich, St. Louis, Missouri, United States.

In order to assess the impact of extractant on the isolated humic acids spectroscopy, chemical and thermal analysis as well as potentiometric titration were used. In addition to demonstrate the potential of examined humic acids as a low-cost reactive barrier material for environmental protection applications of toxic metals, sorption of Cr(VI) on the HAs was carried out using a batch method. The potentiality of HAs to use them in various fields of industry is a well-known fact and the aim of the manuscript was not relevant to the already-known valuable properties of HAs but to demonstrate these potential properties of HAs obtained from polish lignite to use them in modern water treatment.

2. Materials and methods

In Sieniawa opencast mine the 2nd group of Lusatian lignite seams of Early and Middle Miocene age is exploited and represent humic ortholignite of low-coal rank. The characteristic of the Sieniawa lignite used in this study as a source of humic acids are summarized in our study [25,33–34]. Technical humic acids (KHtech) are the commercial humic acids purchased from Sigma-Aldrich. According to Sigma-Aldrich Company, technical HAs are obtained from mines in Germany and is composed of a mixture of decomposing plant parts, peat and soft coal [35].

2.1. Extraction of humic acids

For the extraction of humic acids from the carbon material, analytical techniques typically applied in studies of organic matter and soil humic compounds were used. The review of literature, known analytical techniques and patent descriptions related to humic acids formation from organic materials on the basis of which the extractant was selected was presented and discussed in our other paper [33].

The concept of obtaining humic acids (HAs) from lignite involves two stages. In the first step, lignite was treated with one of extractants: 0.1 M NaOH or 0.1 M $Na_4P_2O_7$ (1:20 w/v) by constant stirring for 12 h. The mixture was then centrifuged at 2,500 x g for 10 min and the soluble supernatant (humic substances – HS) was separated from the insoluble sediment (humin). In a second stage, HAs were precipitated from the extract by acidification of the environment by adding 2 M HCl solution. The coagulation lasted 24 h and then HAs were separated from the soluble fulvic acids (FAs) by centrifugation, as above.

2.2. Characterization of humic acids

The content of carboxylic and phenolic functional groups was estimated by potentiometric acid–base titration. Before measurement, humic acids were dissolved in 20 g 1 M aqueous NaCl solution to assure a constant ionic strength of the solution during titration. The whole volume was transferred into titration vessel. Potentiometric measurements were carried out by using one of the functions of the DL50 Graphix titrator, Mettler Toledo, Schwerzenbach, Switzerland. Titration was performed at 298 K from pH 3 to 11 with standardized 0.1 M solution of NaOH. The equilibrium time between the addition of the titrant and recording the pH was at least 3 min.

Moreover the total acidity (TA) and quantity of carboxyl groups (CA) were analyzed by classical chemical methods. Such methods employ ionic exchange reactions, with $Ba(OH)_2$ to determine total acidity and Ca-acetate to determine carboxylic acidity. Then the suspensions were filtered and the residue was washed with twice distilled water. Filtrate and washing combined were titrated potentiometrically with standard HCl or NaOH, respectively. Acidity of other functional groups (OA) was calculated as difference of total acidity and amount of carboxyl groups.

The specific surface area of humic acids was determined by adsorption–desorption of water vapor in accordance with Polish Standard PN-Z-19010-1. The determination is based upon water vapor adsorption at relative pressure in range from 0 to 0.35 according to BET equation. For the adsorption measurement, vacuum drying apparatus with thermostat is used. The desired water pressure is obtained by using sulphuric acid solutions of different concentrations. The mass of adsorbed water vapor is determined by gravimetric method.

The thermal behavior of samples as a function of temperature was determined by an air flow simultaneous thermal analyzer NETZSCH STA 449 F3 Jupiter®, coupled to QMS 403 Aëolos® quadrupole mass spectrometer in order to detect the gas evolved from the thermal analyzer in the range m/z = 12–64. Thermogravimetric curves were obtained from approximately 50 mg of solid humic acids sample. Measurements were carried out in air atmosphere (30 mL/min) at 5°C/min heating rate in the temperature range of 35°C–800°C. DTA type S sensor type and Al_2O_3 crucibles were used.

Solid-state ^{13}C-NMR spectra of HA samples were obtained on an MSL-300 spectrometer (Bruker, Coventry, UK) operating at 75.482 MHz for ^{13}C. A ^{13}C field strength of 68 kHz was used, corresponding to $\pi/2$ pulse times of 3.7 μs. Samples were spun in zirconium oxide rotors at the magic-angle at a spinning speed of 3 kHz. Based on the areas defined under peaks, the contribution of carbon was calculated: Cal - aliphatic bonds (0–95 ppm), Car – aromatic bonds (95–160 ppm); Clig – aromatic lignin bonds (140–160 ppm); C-COOH – carboxyl groups (160–210 ppm).

The sorption of Cr(VI) on HAs was studied by batch technique. The conditions used for this study have been established according to experiment described in the paper [36]. The method is based on the following assumptions: 0.075 g HAs was equilibrated with 25 mL of the Cr(VI) solution with the initial metal concentration of 1.0 mM at room temperature. The interaction of Cr(VI) with HAs was investigated at different pH values in the range of 2.0–5.0 and pH measurements were performed with an Orion 5 Star model digital pH meter. The solution's pH was adjusted with diluted 0.1 M HNO_3 or 0.1 M NaOH solution. The contact time of HAs with Cr(VI) solutions was set at 24 h and then the phases were separated by filtration and filtrate was collected in a separate beaker. The analysis of Cr(VI) was carried out ICP OES method by using 720/730 Series ICP-OES Spectrometers from Agilent Technologies, Santa Clara, California, United States. The concentration of chromium metal ions was calculated from the change in metal concentration in the aqueous solution before and after equilibrium sorption.

All experiments were carried out three times. The final values are the averages of the measurements repetition.

3. Results and discussion

Active functional groups include: carboxyl (–COOH), hydroxyl (phenol and alcohol –OH), ketone and quinone (= C = O) and methacrylic (–OCH_3). Generally the highest proportion of active humic acid functional groups is carboxyl and phenolic groups, and their content generally determines the total acidity of the preparations.

The content of carboxyl and phenolic groups in tested humic acids determined by the direct potentiometric titration method and chemical methods using the indirect titration technique are presented in Table 1.

For each sample, the pH of the inflexion point was between 7 and 8. These pH values correspond to the phenolic groups. Additional inflection point at about pH 5 can be observed for the sample of humic acids obtained using 0.1 M $Na_4P_2O_7$. This point is attributed to carboxylic groups. Determination of carboxyl group content in samples SN0.1 and KHtech by direct potentiometric titration was impossible, therefore for this purpose a chemical analysis based on the principles of indirect titration was used. For those measurements according to the convention, the content of all acidic functional groups is referred to total acidity (TA), content of carboxylic groups by carboxylic acidity (CA) and the difference is the amount of phenolic groups. Calculating the content of phenolic groups from the difference in total and carboxylic acidity, in the case of humic acids derived from lignite seems to be a mistake and it is, therefore, referred to as the acidity of other functional groups (OA). The most similar results to those obtained for technical humic acids were for SN0.1 and for SP0.1 the total acidity was even higher. The results confirm that the highest content of carboxylic groups is characterized also by humic acids obtained by extraction with 0.1 M $Na_4P_2O_7$. These dependences relate to fact that the extreme extraction conditions can promote some structural alternations in the humic acids including the breakdown of humic macromolecules, especially the destruction of valuable functional groups which indicate the potential of HAs as an agent for the purification of aqueous solutions containing heavy metals.

The presence of these groups in fact determines many properties of humic substances such as hydrophilicity, acidic nature, ion exchange capacities and the possibility of mineral–organic linkages, which are extremely important in affecting the retention and mobility of metal contaminants in aqueous solutions [36,37]. To characterize the organic samples, which have a significant content of functional groups, it seems intentional to determine their specific surface area. This parameter expressed in m^2/g determines the ability of porous substrates to adsorb gases, vapors and ions. The principle of this method is the determination of the initial adsorption–desorption isotherm fragment (in the range of relative pressure of the adsorbate $0 < p/p_0 < 0.35$). Then, based on the assumptions of Brunauer, Emmet, Teller (BET) theory, the specific surface area of the samples was calculated. Table 2 shows the parameters of the BET equation for water vapor adsorption in the pressure range $0 < p/p_0 < 0.35$ and the results of the specific surface area of examined humic acids.

The specific surface area for all humic acids samples is high – 394.4 m^2/g for HAs SN0.1, 370.0 m^2/g for HAs SP0.1 and 371.2 m^2/g for technical humic acids form Sigma-Aldrich. Generally, the specific surface area of organic materials is associated with the physical properties of water, namely the dipole moment and therefore the possibility of creating strong hydrogen bonds with the polar surface functional groups of the tested preparations. The type and amount of functional groups in humic acids is therefore a decisive impact on the

Table 2
Parameters of adsorption–desorption of water vapor in the range of relative pressure of adsorbate $0 < p/p_0 < 0.35$ and the specific surface area of humic acids

Type of sample	C_{BET}	R	S (m^2/g)
SN0.1	102.1	0.999	394.4
SP0.1	36.9	0.998	370.0
KHtech	89.2	0.998	371.2

Table 1
Content of carboxyl and phenolic groups in tested humic acids

Type of sample	Direct potentiometric titration		Indirect titration method		
	C_{OH}	C_{COOH}	Total acidity (TA)	Carboxyl acidity (CA)	Acidity of other functional groups (OA)
	(mmol/g)				
SN0.1	2.41	–	6.98	4.24	2.74
SP0.1	3.45	2.09	7.69	3.99	3.70
KHtech	2.38	–	7.00	4.11	2.89

size of their surface area. The results correlate with the results of humic acids acidity. The highly developed surface area of examined humic acids indicate that using these organic compounds as sorbents in wastewater treatment offer an attractive and inexpensive option for removal of colloidal and dissolved metals. However, it cannot be ruled out that in humic acids – water vapor system, apart from adsorption other processes do not occur, for example, volume vapor absorption or hydration of surface cations, which in consequence can affect the falsification of results.

The linear form of adsorption–desorption isotherms for the tested humic acids is shown in Fig. 1. The BET function for all humic acids samples is straightforward, the correlation coefficient R^2 is high and for all samples is greater than 0.98. The above guidelines indicate the proper conduct of the study and the positive value of the C_{BET} further confirms this fact.

To better understand and determine the relationship between the structure of humic acids and their properties useful from the application point of view, it is necessary to gain more detailed knowledge of their structure nature. One of helpful methods of humic acids analysis is thermal analysis which allows quantitative evaluation of physical changes and chemical reactions occurring in the sample as a function of temperature. Thermo-oxidative behavior of examined humic substances was investigated employing thermogravimetry (TG and DTG curves) and thermal differential analysis (DTA curve). The TG/DTA curves for lignite humic acids were obtained in order to determine their thermal stability, as shown in Figs. 2 and 3. The TG/DTA curves of technical humic acids (KHtech) from Sigma-Aldrich are shown in Fig. 4. Curves TG/DTA are shown with the results of the gas phase analysis of the sample – the observed changes in CO_2 concentration ($m/z = 44$) and H_2O ($m/z = 18$).

All TG/DTA curves for lignite humic acids were characterized by an endothermic peak at a temperature range of 100°C–120°C. This peak is the result of dehydration and the difference in the amount of accompanying mass loss results from the different degree of water binding through the sample. The first significant temperature range for the transformation of organic matter is attributed to a range of 200°C–400°C and is related to the degradation of less thermally stable structures, generally characterized by a less

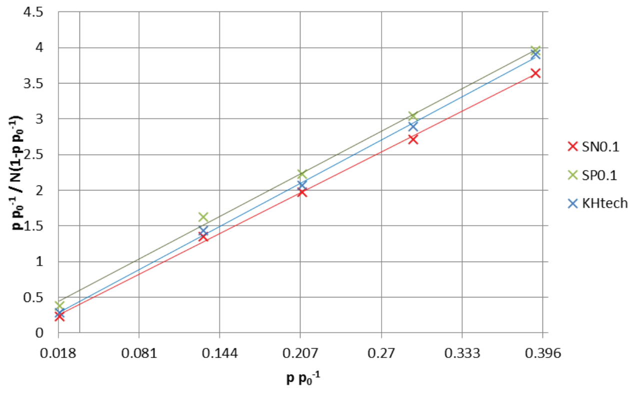

Fig. 1. Linear form of adsorption–desorption isotherms for the tested humic acids.

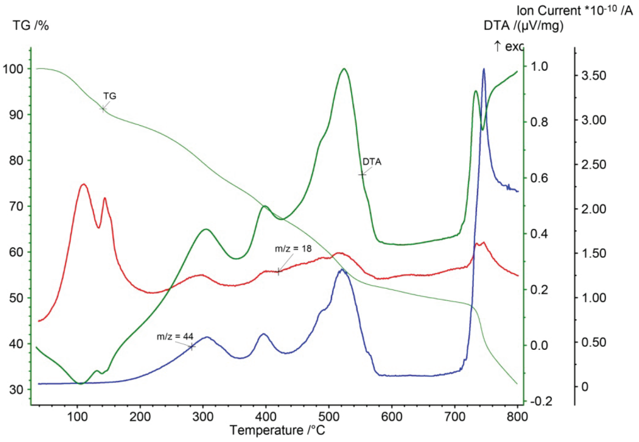

Fig. 2. TG/DTA curves of humic acids obtained from lignite Sieniawa with 0.1 M NaOH and the change in the concentration of CO_2 ($m/z = 44$) and H_2O ($m/z = 18$) in the gas phase of the sample.

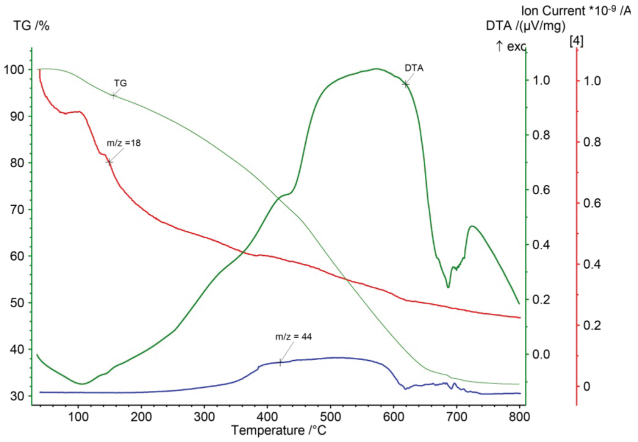

Fig. 3. TG/DTA curves of humic acids obtained from lignite Sieniawa with 0.1 M $Na_4P_2O_7$ and the change in the concentration of CO_2 ($m/z = 44$) and H_2O ($m/z = 18$) in the gas phase of the sample.

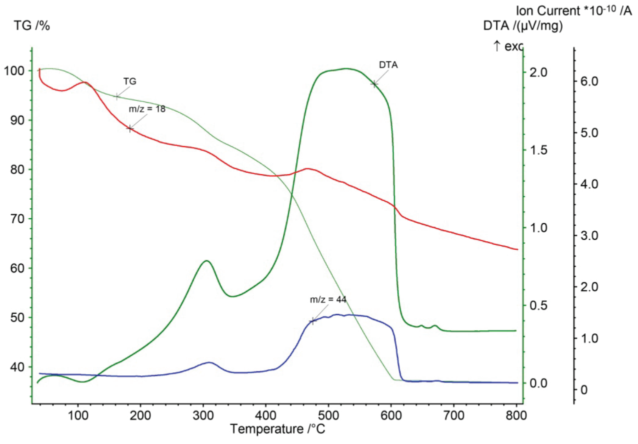

Fig. 4. TG/DTA curves of technical humic acids from Sigma-Aldrich Company and the change in the concentration of CO_2 ($m/z = 44$) and H_2O ($m/z = 18$) in the gas phase of the sample.

condensed structure. The loss of mass in this temperature range is attributed to changes such as degradation of carbohydrates, dehydration of aliphatic structures and decarboxylation of carboxylic groups. These changes in the DTA graph are reflected in the form of exothermic peaks at a temperature close to 300°C especially sharp for samples of humic acids obtained using 0.1 M NaOH solution. The resulting mass loss for this sample was amounted to 14.03% and it can be attributed to the loss of simple hydrocarbon compounds. Changes occurring at temperatures higher than 400°C affect the degradation of more condensed structures and oxidation of aromatic components and breakdown of C–C bonds. These reactions are probably related to the occurrence of long-chain hydrocarbons and nitrogen compounds. According to the literature above 500°C a pyrolysis of aromatic components of lignin and other polyphenols occurs and the aromatic core of humic acids structure is presumably destroyed. Exothermic effect occurring at temperatures above 600°C is probably due to high-temperature changes associated with polycondensation and depolymerization reactions [38–41].

Comparing TG/DTA curves for KHtech with those obtained by extraction from lignite, a relatively high similarity with sample SP0.1 was noted. For these samples, the TG/DTA curves were characterized by two similar exothermic effect at about 100°C and between 400°C and 600°C. The mass loss for KHtech at mentioned temperature range were, respectively, $m_1 = 6.28\%$, $m_2 = 47.67\%$ and for SP0.1 $m_1 = 5.84\%$, $m_2 = 42.16\%$. The basic difference between the samples was noted in the range of 200°C–400°C, in which a clear peak was observed only for the KHtech sample and also for humic acids obtained by using 0.1 M NaOH. The mass loss of humic acids samples in the temperature ranges is shown in Table 3.

The thermal analysis of humic acids was 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 derivatograms. For all examined samples, an intense increase in CO_2 concentration can be observed at the temperature ranges of the characteristic exothermic peaks, which confirms the distribution of carbon structures both aliphatic and aromatic. Analysis of the gas phase for examined samples showed also an increase in H_2O concentration near 100°C.

Table 3
Thermal analysis (thermic effects) of humic acids samples

Type of sample	Maximum decomposition temperature (°C)	Temperature range (°C)	Mass loss (%)	Residue (%)
SN0.1	101.2	40–180	11.26	31.60
	295.6	180–340	14.03	
	511.6	340–570	22.31	
	744.7	570–800	20.80	
SP0.1	104.7	40–160	5.84	32.37
	319.7	160–380	17.26	
	479.5	380–670	42.16	
	683.3	670–800	2.37	
KHtech	101.6	40–180	6.28	36.36
	300.9	180–340	9.23	
	464.9	340–625	47.67	
	669.8	625–800	0.46	

More specific information concerning the structure of the HA could be obtained from ^{13}C NMR spectroscopy. Fig. 5 shows the solid-state ^{13}C NMR spectra of humic acids extracted from lignite using different solutions and for technical humic acids (KHtech) from Sigma-Aldrich. ^{13}C NMR spectra of humic acids can be divided into three basic characteristic of these compounds ranges of chemical shifts: 0–95 ppm – carbon in aliphatic bonds (Cal), 95–160 ppm – including aromatic carbon (Car), 160–200 ppm – carbon in carboxyl groups (C–COOH).

^{13}C NMR spectra of humic acids obtained from Sieniawa lignite generally are characterized by only one clear peak at around 30 ppm corresponding to aliphatic carbon (Cal), in particular the methyl and methylene groups. There is also some absorption intensity in the range of 95–160 ppm. However, it is not possible to distinguish in this area the characteristic peak, and the intensity of absorption in this range of chemical shifts is significantly lower than for the range of 0–95 ppm. This proportion informs about the superiority in these preparations aliphatic structures over aromatic, which is characteristic of "young" humic acids. Range between 95 and 160 ppm corresponds to aromatic carbon bonds (Car) and may indicate that examined humic acids are characterized by less condensed structures. Comparing preparations obtaining from lignite, we can observe that humic acids extracted with 0.1 M NaOH are less condensed than those extracted with 0.1 M $Na_4P_2O_7$. SP0.1 sample is characterized by a certain amount of carboxyl groups, as

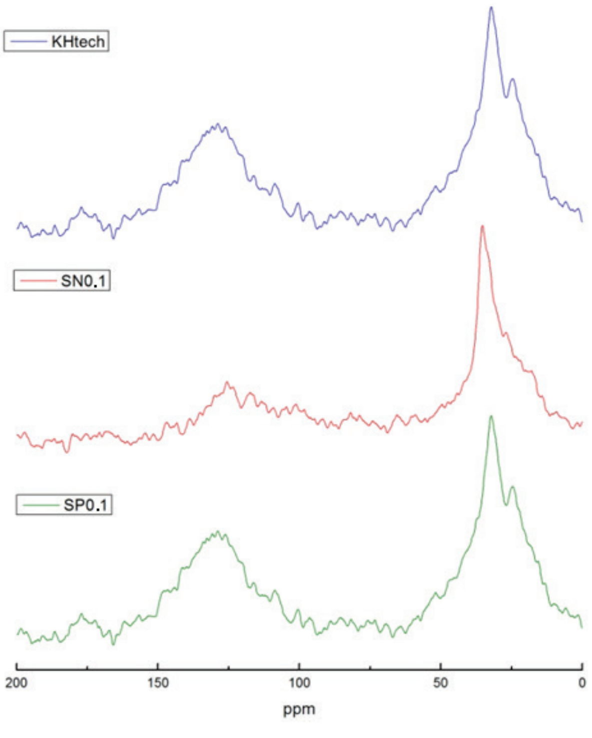

Fig. 5. ^{13}C NMR spectra of examined humic acids samples.

evidenced by a slight increase in absorption intensity in the range of 160–190 ppm. It can suggest that humic acids obtained from lignite using solution of $Na_4P_2O_7$ have good sorption properties and from this reason this kind of humic acids can be valuable material in water treatment. Therefore, process of obtaining humic acids from organic materials should be characterized by such parameters which allow to achieve high efficiency of humic acids isolation and simultaneously preserve their bioactive structures and obtain products of exceptional quality. For the KHtech sample, the most similar ^{13}C NMR spectrum was obtained for lignite humic acids using 0.1 M $Na_4P_2O_7$. This fact confirms the contents of the individual structures calculated based on the area under the peaks in the characteristic for humic substances range of chemical shifts (Table 4).

However, interpretation of the ^{13}C NMR spectra is limited to determining the number of equivalent ^{13}C atoms and defining based on their chemical shift, what type of molecular structure elements they belong to. Therefore, it is recommended to treat NMR results as reflecting the statistical conditions and to determine the functional groups content in humic acids using more precise methods such as, for example, potentiometric titration.

Fig. 6 shows the effect of pH on the sorption of Cr(VI) by HAs obtained from polish lignite. The sorption was conducted from solutions of an initial pH from 2.0 to 5.0. It is generally known that –COOH groups of HAs form strong complex – heterocyclic chelates with Cr(VI) ions depending on the pH of the mobile phase [42,43]. Opinions how complexation between HAs and metal ions occur were described briefly in a study by Arslan et al. [36]. According to this paper, Cr(VI) may exist in the aqueous phase in different anionic forms, such as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) or hydrogen chromate ($HCrO_4^-$), with total chromate concentrations and pH dictating which particular chromate species is predominant. Similarly to the results presented in this paper Cr(VI) sorption on humic acids samples increased with a decreasing pH. It was observed that the removal efficiency of Cr(VI) decreased from 75.4% to 62.6% for HAs SN0.1, from 79.8% to 66.5% for HAs SP0.1 and from 70.1% to 65.4% for technical HAs with the rise of pH form 2 to 5. The increase of Cr(VI) sorption at acidic pH is probably due to the electrostatic forces between positively charged groups of humic acids surface and the $HCrO_4^-$ anion, which is the dominant species at low pH and it is the largest for HAs SP0.1. Consequently we could expect that the decrease of the sorption with increasing pH is caused by decrease of electrostatic forces and the competitiveness between the chromium anionic species and OH^- ions. From these assumptions, it can be suggested that Cr(VI) removal takes place by physical adsorption [36]. But above pH 3.5 according to Fig. 6 sorption degree is considerably reduced so it suggests that other mechanism such as physical adsorption on the surface of sorbent could have taken an important role in sorbing Cr(VI) [36]. The lower values of the Cr(VI) sorption degree compared with those presented in the cited reference may be due to the fact that the humic acids used in the study were not thoroughly purified. In the perspective of their use in water treatment, this stage should be taken into account. Moreover humic acids as a potential component should be before using subjected to immobilization test on a solid support to avoid the HAs leaching from the bed.

Table 4
Carbon distribution (%) in resonance intervals (ppm) ^{13}C NMR spectra of humic acids

Type of extractant	SN0.1	SP0.1	KHtech
Range (ppm)	Carbon distribution (%)		
0–95	78.9	58.5	59.35
95–160	18.2	37.9	38.55
140–160	2.42	8.60	7.93
160–190	2.40	3.54	2.10

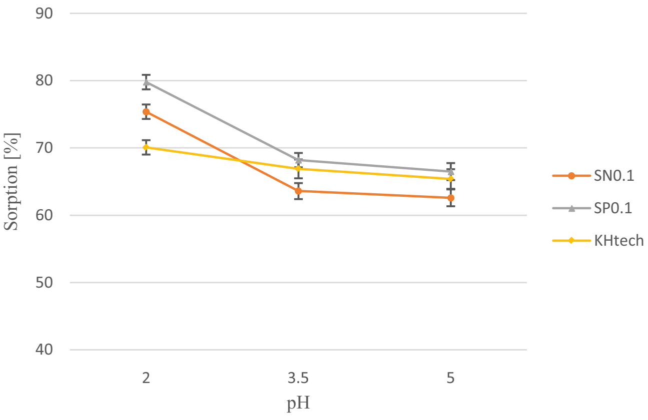

Fig. 6. Effect of pH on the sorption of Cr(VI) by HAs obtained from polish lignite depending on extractant used for their isolation.

4. Conclusions

In Poland due to economic and technological developments it seems real to use lignite as a material for humic acids preparation. In structure of humic acids derived from lignite, Sieniawa dominated the aliphatic connections. Their participation in HAs obtained by using 0.1 M NaOH is higher and amounts to 78.9%. For sample obtained using 0.1 M $Na_4P_2O_7$ participation of aliphatic units amounts to 58.5%. Less destructive compounds such as $Na_4P_2O_7$ guarantee good sorption properties of the product. The results confirm that highest content of all acidic functional groups is characterized by HAs obtained by extraction with 0.1 M $Na_4P_2O_7$ and it was 7.69 mmol/g. From ^{13}C NMR spectra, we also see that HAs SP0.1 contain more functional groups – 3.54% of carboxylic groups, assigned to peak in the range of 160–190 ppm. The specific surface area for both humic acids samples was high from 370.0 to 394.4 m^2/g and correlate with the results of humic acids acidity. The highly developed specific surface area of HAs SP0.1 and the presence of hydrophilic functional groups determining their specific sorption and ion exchange properties which allows them potentially to adsorb heavy metals or other pollutants, have confirmation in the results of Cr(VI) sorption study. It was observed that the highest removal efficiency of Cr(VI) – 79.8% for HAs SP0.1 was achieved at pH 2. Therefore, this kind of humic acids can be successfully used for the adsorption of Cr(VI) in water treatment applications.

The mechanism for contaminant removal of humic acids is believed to be a combination of ion-exchange and chelation/complexation and these properties of examined HAs indicate the possibility of using them as sorbents in water treatment as an attractive and inexpensive alternative for the removal of colloidal and dissolved metals. However, the potential humic acids as a component in modern water treatment should be before using, insolubilized and/or immobilized on a solid support to avoid the HAs leaching from the bed, in which the HAs properties would be used. It is important, however, that after cross-linking all the functional groups responsible for contaminant removal to have been retained. This problem is very important and requires further research.

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References

[1] J.F. Blais, S. Dufresne, G. Mercier, State of the art of technologies for metal removal from industrial effluents, J. Water Sci., 12 (1999) 687–711.

[2] B. Sancey, G. Trunfio, J. Charles, J.F. Minary, S. Gavoille, P.M. Badot, G. Crini, Heavy metal removal from industrial effluents by sorption on cross-linked starch, J. Environ. Manage., 292 (2011) 765–772.

[3] G. McKay, M.J. Bino, A.R. Altamemi, The adsorption of various pollutants from aqueous solutions on to activated carbon, Water Res., 19 (1985) 491–495.

[4] A. Bhatnagar, M. Sillanpää, Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment - a review, Chem. Eng. J., 157 (2010) 277–296.

[5] E. Lorenc-Grabowska, G. Gryglewicz, Adsorption of lignite-derived humic acids on coal-based mesoporous activated carbons, J. Colloid Interface Sci., 284 (2005) 416–423.

[6] C. Selomulya, V. Meeyoo, R. Amal, Mechanisms of Cr(VI) removal from water by various types of activated carbons, J. Chem. Technol. Biotechnol., 74 (1999) 111–122.

[7] J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla, M. Sanchez-Polo, Waste materials for activated carbon preparation and its use in aqueous phase treatment: a review, J. Environ. Manage., 85 (2007) 833–846.

[8] L. Monser, N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium, and cyanide from wastewater, Sep. Purif. Technol., 26 (2002) 137–146.

[9] S.P. Dubey, K. Gopal, Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: a comparative study, J. Hazard. Mater., 145 (2007) 465–470.

[10] E.A. Ghabbour, G. Davies, Humic Substances: Molecular Details and Applications in Land and Water Conservation, Taylor & Francis, Inc., New York, 2005.

[11] F.J. Stevenson, Humus Chemistry: Genesis, Composition, Reactions, 2nd ed., Wiley, New York, 1994.

[12] E. Tipping, Cation Binding by Humic Substances, Cambridge University Press, Cambridge, 2002.

[13] A.G. Proidakov, Humic acids from mechanically treated coals: a review, Solid Fuel Chem., 43 (2009) 9–14.

[14] V. Romaris-Hortas, A. Moreda-Pineiro, P. Bermejo-Barrera, Application of microwave energy to speed up the alkaline extraction of humic and fulvic acids from marine sediments, Anal. Chim. Acta, 602 (2007) 202–210.

[15] T. Andjelkovic, J. Perovic, M. Purenovic, S. Blagojevic, R. Nikolic, D. Andjelkovic, A. Bojic, Acidity of humic acid related to its oxygen-containing functional groups, Maced. J. Chem. Chem. Eng., 25 (2006) 131–137.

[16] M. Fukushima, S. Tanaka, H. Nakamura, S. Ito, Acid-base characterization of molecular weight fractionated humic acid, Talanta, 43 (1996) 383–390.

[17] J.C. Masini, G. Abate, E.C. Lima, L.C. Hahn, M.S. Nakamura, J. Lichtig, H.R. Nagatomy, Comparison of methodologies for determination of carboxylic and phenolic groups in humic acids, Anal. Chim. Acta, 364 (1998) 223–233.

[18] M. Fuentes, R. Baigorri, G. González-Gaitano, J.M. García-Mina, New methodology to assess the quantity and quality of humic substances in organic materials and commercial products for agriculture, J. Soil Sediments 18 (2018) 1389–1399.

[19] L.P. Canellas, F.L. Olivares, N.O. Aguiar, D.L. Jones, A. Nebbioso, P. Mazzei, A. Piccolo, Humic and fulvic acids as biostimulants in horticulture, Sci. Hortic., 196 (2015) 15–27.

[20] M. Widera, An overview of lithotype associations of Miocene lignite seams exploited in Poland, Geologos, 422 (2016) 213–225.

[21] A. Pietraszewski, Polish lignite mining industry, Brown Coal, 79 (2012) 54–59 (in Polish).

[22] L. Doskočil, J. Burdíková-Szewieczková, V. Enev, L. Kalina, J. Wasserbauer, Spectral characterization and comparison of humic acids isolated from some European lignites, Fuel, 213 (2018) 123–132.

[23] A. Giannouli, S. Kalaitzidis, G. Siavalas, A. Chatziapostolou, K. Christanis, S. Papazisimou, C. Papanicolaou, A. Foscolos, Evaluation of Greek low-rank coals as potential raw material for the production of soil amendments and organic fertilizers, Int. J. Coal Geol., 77 (2009) 383–393.

[24] M. Piwocki, Extent and correlations of main groups of the Tertiary lignite seams on Polish platform area, Geol. Rev., 40 (1992) 281–286 (in Polish).

[25] M. Widera, Changes of the lignite seam architecture — a case study from Polish lignite deposits, Int. J. Coal Geol., 114 (2013) 60–73.

[26] S.A. Semenova, Y.F. Patrakov, M.V. Batina, Ozonization of humic acids in brown coal oxidized in situ, Solid Fuel Chem., 42 (2008) 268–273.

[27] M. Skybova, L. Turcaniova, S. Cuvanova, A. Zubrik, S. Hredzak, L. Hudymacova, Mechanochemical activation of humic acids in the brown coal, J. Alloys Comp., 434 (2007) 842–845.

[28] A. Jezierski, F. Czechowski, M. Jerzykiewicz, J. Drozd, EPR investigations of structure of humic acids from compost, soil, peat and soft brown coal upon oxidation and metal uptake, Appl. Magn. Reson., 18 (2000) 127–128.

[29] H. Martyniuk, J. Więckowska, Adsorption of metal ions on humic acids extracted from brown coals, Fuel Process. Technol., 84 (2003) 23–36.

[30] E.G. Abramov, A.A. Bezzubov, Electrosorptive separation of humic substances, J Water Chem. Technol., 29 (2007) 125–130.

[31] H.G. Sanjay, A.K. Fataftah, D.S. Walia, K.C. Srivastava, K.C., In: E.A. Ghabbour, G. Davies, Eds., Understanding Humic Substances: Advanced Methods, Properties and Applications, The Royal Society of Chemistry, Cambridge, 1999, pp. 241–255.

[32] H.G. Sanjay, K.C. Srivastave, D.S. Walia, Development of HUMASORB™, a Lignite Derived Humic Acid for Removal of Metals and Organic Contaminants from Groundwater, Proceedings of the Environmental Technology Through Industry Partnership Conference, Vol. 2, 1995, pp. 411–424.

[33] M. Huculak-Mączka, J. Hoffmann, K. Hoffmann, Evaluation of the possibilities of using humic acids obtained from lignite in the production of commercial fertilizers, J. Soils Sediments, 18 (2018) 2868–2880.

[34] J. Macuda, A. Nodzeński, M. Wagner, L. Zawisza, Sorption of methane on lignite from Polish deposits, Int. J. Coal Geol., 87 (2011) 41–48.

[35] R.T. Lamar, K.H. Talbot, Critical Comparison of Humic Acid Test Methods, Comm. Soil Sci. Plant Anal., 40 (2009) 2309–2322.

[36] G. Arslan, S. Edebali, E. Pehlivan, Physical and chemical factors affecting the adsorption of Cr(VI) via humic acids extracted from brown coals, Desalination, 255 (2010) 117–123.

[37] A.K. Pandey, S.D. Pandey, V. Misra, Stability constants of metal - humic acid complexes and its role in environmental detoxification, Ecotoxicol. Environ. Saf., 47 (2000) 195.

[38] M. Klavins, L. Ansone, J. Tjutrins, I. Silamikele, O. Purmalis. Differential thermal analysis of peat and peat humic acids in relation to their origin, In: M. Klavins, Ed., Mires and Peat, University of Latvia Press, Riga, 2010, pp. 207–214.
[39] A. Iordanidisa, A. Georgakopoulosa, K. Markovab, A. Filippidisa, A. Kassoli-Fournaraki, Application of TG-DTA to the study of Amyntean lignites, northern Greece, Thermochim. Acta, 371 (2001) 137–141.
[40] O. Francioso, D. Montecchio, P. Gioacchini, C. Ciavatta, Thermal analysis (TG-DTA) and isotopic characterization (13C-15N) of humic acids from different origins, Appl. Geochem., 20 (2005) 537–544.
[41] M.T. Dell'Abate, A. Benedetti, A. Trinchera, C. Dazzi, Humic substances along the profile of two Typic Haploxerert, Geoderma, 107 (2002) 281–296.
[42] C. Namasivayam, S. Senthilkumar, Adsorption of Copper(II) by "Waste" Fe(III)/Cr(III) Hydroxide from Aqueous Solution and Radiator Manufacturing Industry Wastewater, Sep. Sci. Technol., 34 (1999) 201–217.
[43] E. Pehlivan, G. Arslan, Removal of metal ions using lignite in aqueous solution - Low cost biosorbents, Fuel Process. Technol., 88 (2007) 99–106.