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ASSESSMENT OF EFFICIENCY OF HUMIC ACIDS EXTRACTION PROCESS USING DIFFERENT FINENESS OF LIGNITE

OCENA WYDAJNOŚCI EKSTRAKCJI KWASÓW HUMINOWYCH Z WĘGLI BRUNATNYCH O RÓŻNYM UZIARNIENIU

Abstract: Humic acids are a group of distinctive organic compounds, which are created in complicated biochemical processes, such as oxidation, condensation and polymerization of high-molecular products of plant and animal residue decomposition. They facilitate plants micronutrient uptake, improve soil structure, porosity and consequently aeration, water retention and also viscosity, firmness and creating aggregate structures. The aim of the research was to determine efficiency of humic acids extraction process, using different kinds and fineness of lignite. Stronger fines size reduction provides growth of active surface subjected to extractant treatment and better porosity of mass subjected to extraction, so as the lignite fineness decreasing the increase of efficiency of humic acids production is expected. Finding optimum fineness, which is a compromise between extraction efficiency and raw material grinding costs, will enable economical production of humic acids fertilizer agents.

Keywords: humic acids, extraction process efficiency, fineness

Organic substances in soil undergo continuous transformations. Their kind and intensity depends on flora, soil fauna, microorganisms and other physical and chemical properties. Two main directions of changes, which organic matter is subjected to, are mineralization and humification. In fertilizer point of view, the most interesting are reactions that lead to formation of humus compounds, which fulfill a very important role in soil, because they influence on many of its properties like fecundity and productivity. Only 20–25 % of organic matter undergo this kind of transformations and they are much more complicated than matter mineralization process. Humification is based on decay and synthesis of organic compounds as well as polymerization and

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condensation of forming products. This process is not fully explored, because of its complexity. Humus created in this way mainly consists of *humic acids* (HA), *fulvic acids* (FA) and humins. Fulvic acids are soluble in water independently of reaction and characterized by yellow or brown and yellow colour. Humins are black and completely insoluble in water. However, the most interesting, in fertilizer point of view, are humic acids which are dark-brown or black humus fraction insoluble in acidic environment [1–3].

Humic acids are polymers built of aromatic core containing phenol or nitrogen in cyclic form. The core binds with sugars, peptides, amino acids, acids and other aliphatic compounds [1, 2]. Their complex, condensed, irregular and amorphous structure results in chemical and biological decomposition resistance [3, 4]. The majority of widely accepted theories claim that humic acids are high-molecular polymers but the newest researches indicate that this structure consist of low-molecular compounds creating very big associated molecules. This theory does not stand in contradiction to earlier, commonly accepted view. It only suggests that humic acids are not built of regularly repeated monomeric units that form polymer, but miscellaneous molecules physically connected with each other into irregular structure [3, 4].

Use of humic acids

Humic acids have many applications, among others, as dyes, wood hardening agents and they are also used in veterinary medicine or synthetic polymers production [5]. However, they are used the most commonly in agriculture, because of their colloidal character and huge active surface giving them fine adsorptive properties [6]. In natural environment, humic acids mould proper structure of soil, facilitating water retention, improving porosity and consequently aeration. Moreover, the dark colour of humic acids influences on substratum albedo, helping to absorb adequate amount of solar radiation. Adsorptive features 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 [6–10].

Sources of humic acids

The above-mentioned properties are extremely attractive for fertilizer industry, because process of creating humus in soil lasts incredibly long. In favourable conditions forming 1 cm^3 of humus takes even a few hundred years, while its influence on the ground fertility is inestimable. That is why new sources of humic acids are prospected. For instance, brown coal, peat, biomass, some kinds of soils or even marine sediments are used [11]. One of the richest source of humic compounds are leonardites, an intermediate form between peat and lignite. However, access to their deposits is quite limited, because they occur mainly in the United States of America and that is why other raw materials are usually used. There are many ways of obtaining humic acids. Some of them are based on underground extraction of humic acids using particular microorganisms, but the vast majority includes mining the material and industrial extraction. Using brown coal for that purpose may be very perspective direction. This fossil fuel, because of its dampness, volatile matter and sulfur compounds content influences very unfavorably on the atmosphere during combustion. More especially as in many countries this coal is used almost entirely in power industry. Admittedly the structure of humic compounds depends on bioclimatic conditions in which they were formed, yet there are no significant differences between humus created in soil and this one from coal [6–12].

Influence of chemical and physical factors on humic acids extraction process

Obtaining humic acids from a lignite or some other sources is possible thanks to specific properties of humic compounds, that is their solubility. Humins are insoluble in the whole pH range. Therefore, adding alkaline extractant to the raw material, mixture of humic and fulvic acids is received. Taking advantage of humic acids insolubility in acidic environment next allows to precipitate them by reducing reaction of the mixture. Many different extractants are used to obtain humic acids. Starting with the most aggressive like sodium hydroxide or potassium hydroxide, to more mild compounds among which sodium pyrophosphate and sodium tripolyphosphate are used. NaOH and KOH provide higher efficiency of extraction process, however they are suspected of simultaneous partial destruction of obtained compounds structure and contribution in contaminating product with other compounds [13, 14]. Less destructive are compounds like $Na_4P_2O_7$ or $Na_5P_3O_{10}$, but they guarantee higher purity of the product concurrently lowering the productivity [11, 15, 16]. Course of the extraction also depends on temperature of the process, time and additional factors, like speeding up the extraction with ultrasonic waves [2, 17, 18].

Many methods, patents and industrial standards concerning humic acids extraction from lignite strictly describe fineness of used raw material, which clearly suggest that it influences on course and efficiency of the process [3, 9]. Economic factors also determine the character of humic acids production on a mass scale. Therefore, it is essential to define optimum coal fineness, which provides the biggest profit after calculating extraction process efficiency and raw material grinding costs.

Materials and methods

The aim of research was to determine efficiency of humic acids extraction process, using different fineness of lignite. Lignite from Konin coal basin and Belchatow coal basin was analysed. Brown coal is an intermediate form between peat and hard coal, formed in neogen in Cenozoic. It is almost entirely used in power industry by burning in thermal power station next to the strip mine, because of its low rank of coal and high dampness. The alternative way of using this fuel, protecting the atmosphere from harmful chemical compounds emission, may be production of humic acids used next in agriculture.

Obtained this way humic acid in the form of gel, after desiccation and grinding down can be used separately as fertilizing agent or can be an additive to other fertilizers.

Factories in the United States and Germany already conduct this kind of production and in Poland fertilizing agents with humic acids addition are also available.

Four extractants were used in the research: sodium hydroxide, potassium hydroxide, sodium pyrophosphate and *sodium tripolyphosphate* (TPS), which were added to samples of four different fineness: 0.2 mm; 0.63 mm; 1.0 mm and 2.0 mm. After carrying out the extraction, carbon content was determined in direct extract including humic and fulvic acids and in pure humic acids. Carbon determination was made in accordance with modified Alten method.

Samples of given fineness were subjected to specific extractants: 0.1 M NaOH; 0.1 M KOH; 0.1 M $Na_4P_2O_7$; 0.1 M TPS in a proportion 1:20. Then mixtures were thoroughly blended, plugged with rubber stoppers, put into a shaker for 2 hours and left till next day. Obtained extracts were centrifuged and filtered to flasks from which there were taken samples for determination of organic carbon (C_{org}) in direct extract (HA + FA). The solutions which remained in flasks were subjected to 2 M H_2SO_4 and left for 24 hours in order to precipitate humic acids, which were filtered subsequently. After dissolving humic acids gel on filters using 2 % Na_2CO_3, samples of organic carbon in humic acids (HA) were taken for further analysis.

Carbon content in samples was determined in accordance with Alten method, which is based on oxidation of organic carbon with 0.34 M potassium dichromate(VI) in the presence of sulfuric acid during 3 hours heating in boiling water bath. Modification of this method is based on using Mohr salt and ferroin sulfate as an indicator for back titration of potassium dichromate(VI), while in the original method iodometry is used for this purpose.

Results and discussion

After analyzes and appropriate calculations following results were obtained (Table 1).

Based on these experiment results following conclusions may be drawn: For both lignite from Konin coal basin, and from Belchatow coal basin and independently of used extractant type, the efficiency of the process, expressed in organic carbon content in direct extract and humic acids, decreases as the fineness of raw material increases. Presumably, stronger fines size reduction provides growth of active surface subjected to extractant treatment and results in increase of humic acids extraction process efficiency. Direct extract has higher organic carbon content, because apart from humic acids it also includes fulvic acids, which are an additional source of organic carbon. The proportion between humic and fulvic acids amount is usually similar for each fineness of raw material and for both products analogous falling tendency is observable when fineness is growing. Furthermore, it is noticeable, that the most humic acids may be obtained when using sodium hydroxide for extraction, a bit less utilizing potassium hydroxide, whereas the least using sodium pyrophosphate or sodium tripolyphosphate. The effectiveness of the two last extractants is similar for each type of brown coal, at the same time it is worth stressing that for raw material from Konin coal basin sodium pyrophosphate turns out to be better, while lignite from Belchatow coal basin provides higher efficiency when using TPS for extraction. It is probably caused by the structure

Table 1

Organic carbon content in direct extract and humic acids obtained from lignite depending on fineness

Extractant type	Lignite fineness [mm]	C_{org} content in direct extract (HA+FA) [%]		C_{org} content in humic acids (HA) [%]	
		Konin	Belchatow	Konin	Belchatow
NaOH	0.2	56.2	45.4	41.9	19.2
	0.63	55.6	42.9	34.6	15.3
	1.0	48.5	37.2	32.0	14.5
	2.0	49.1	13.1	30.7	12.8
KOH	0.2	45.6	37.4	36.3	17.4
	0.63	41.0	36.6	27.3	14.5
	1.0	40.4	40.9	30.4	12.3
	2.0	39.7	26.4	19.4	12.2
$Na_4P_2O_7$	0.2	37.9	26.6	22.1	12.9
	0.63	36.5	15.9	17.9	12.3
	1.0	37.1	15.5	13.1	12.2
	2.0	37.2	9.4	15.5	8.0
TPS	0.2	31.5	28.8	19.3	14.2
	0.63	24.6	16.7	17.8	12.5
	1.0	26.2	15.7	13.2	12.0
	2.0	29.6	18.4	7.5	11.0

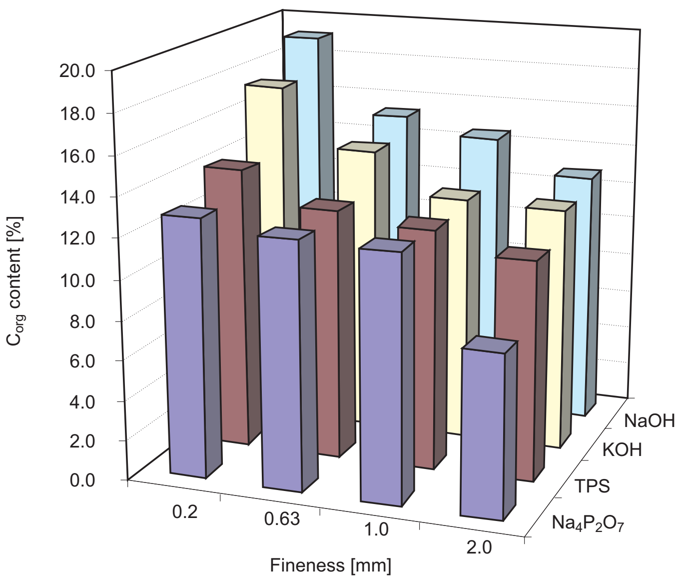

Fig. 1. Organic carbon content in humic acids obtained from lignite using different extractants

and composition of each lignite type and consequently different chemical affinity towards extractants. However, using hydroxides in this process, it is vital to remember about already mentioned destructiveness of NaOH and KOH, which may artificially inflate the efficiency of the process, due to additional impurities extracted form brown coal with the main product. The last thing worthy of attention is that lignite from Konin is richer in humic acids than coal from Belchatow.

Conclusions

The carried out researches proved that lower fineness of the raw material, lignite in this case, causes the increase of humic acids extraction process efficiency. The differences are more noticeable for brown coal from Konin, which shows that even 20 % increase in efficiency level is possible while reducing fines size from 0.63 mm to 0.2 mm. This tendency is probably connected with growth of active surface subjected to extractant treatment. Furthermore, the kind of chemical compound used in extraction is essential. Sodium hydroxide and potassium hydroxide provides higher efficiency of the process but at the cost of obtained humic acids quality. However, sodium pyrophosphate and TPS are less aggressive substances, so using them results in smaller amount of product, but purer and with better preserved structure. That is why it is important to define advisable quality of humic acids while choosing extractant. For instance, if the product is intended for using as a fertilizing agent mixed with other compounds, then it is reasonable to apply extractants obtaining a lot of humic acids, but partially impure, whereas using sodium pyrophosphate or TPS is recommended when high quality and purity of the product is required. Therefore, knowing raw material grinding costs, individual for each factory, and comparing them with the price of obtained product and its application, allows to estimate profitability of lignite grinding and find the best extractant type.

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OCENA WYDAJNOŚCI EKSTRAKCJI KWASÓW HUMINOWYCH Z WĘGLI BRUNATNYCH O RÓŻNYM UZIARNIENIU

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Abstrakt: Kwasy huminowe są grupą specyficznych związków organicznych, które powstają w skomplikowanych procesach biochemicznych, takich jak utlenianie, kondensacja oraz polimeryzacja wysokomolekularnych produktów rozkładu resztek pochodzenia roślinnego i zwierzęcego. Związki te ułatwiają przyswajanie mikroelementów przez rośliny, poprawiają strukturę gleby, wpływają korzystnie na jej porowatość, a tym samym napowietrzenie, retencję wodną oraz lepkość, zwięzłość i tworzenie struktur agregatowych gleb. Celem pracy było określenie wydajności ekstrakcji kwasów huminowych z różnych rodzajów węgla brunatnego, w zależności od jego uziarnienia. Większe rozdrobnienie surowca gwarantuje wzrost powierzchni aktywnej podlegającej działaniu ekstrahenta oraz zapewnia większą porowatość masy poddawanej ekstrakcji, zatem spodziewany jest wzrostu wydajności produkcji kwasu huminowego w miarę zmniejszania uziarnienia węgla brunatnego. Określenie optymalnego sortymentu, będącego kompromisem pomiędzy wydajnością ekstrakcji a kosztami rozdrobnienia surowca, pozwoli na ekonomiczną produkcję środka nawozowego, jakim jest kwas huminowy.

Słowa kluczowe: kwasy huminowe, wydajność procesu ekstrakcji, uziarnienie