DOI: 10.2428/ecea.2020.27(1-2)1 ECOL CHEM ENG A. 2020;27(1-2)

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ASSESSMENT OF THE EFFICIENCY OF HUMIC ACIDS EXTRACTIONS WITH FERTILIZER COMPONENTS

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Abstract: Humic substances are widely applied in many branches of the industry. Their most well-known usage are agricultural and horticultural markets. A popular method of obtaining of mentioned compounds with satisfactory efficiency is an alkaline extraction of them from organic raw materials like peat, leonardite or lignite. The growing use of humic acids preparations is conditioned by improvement of physical, chemical and biological properties of soils. Despite that fact, the use of mineral fertilizers still dominates. Therefore, it seems interesting to produce agents containing both humic substances and traditional fertilizing elements. Such products could be applied as soil improvers. For that reason we have modified the International Humic Substances Society (IHSS) method of humic substances extraction by changing types of extractants and other solutions into solutions of main macroelements (NPK) for plants. The aim of this research was to determine the efficiency of humic acids extraction from polish peat depending on process temperature, its duration and concentration of extractant.

Keywords: fertilizer extractants, humic acids, extraction, peat

Introduction

The growing global population leads to the huge demand for the food production, which may be obtained by various methods. Genetic modification of organisms, the use of fertilizers, as well as the improvement of soil properties can be distinguished. The fertilizer industry is a large-scale chemical production and it is one group of major

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inorganic chemical technology processes. The application of fertilizers is an important source of macronutrients and micronutrients for plants such as nitrogen, potassium, phosphorus, manganese, copper or zinc. Despite the use of fertilizers it may not be sufficient enough to produce the required amount of food. Years of conducting many agricultural techniques and plants cultivation can lead to decrease of soil quality. For that reason, it is worth applying some soils improvers that contain an important soil component – organic humic substances [1–6].

Humic substances most often occur in the natural environment as part of aquatic and terrestrial systems, but also as sediments. The soil organic matter, the source of which are e.g. plants remains, may be subject to two types of change processes: a mineralisation and a humification. The mineralisation process is a breakdown of such substances and a production of simple inorganic chemical compounds. The humification process leads to the formation of more complex organic structures like humic substances. For industrial purposes humic substances may be also obtained from certain types of organic raw materials: peat, leonardite and lignite [7, 8].

Humic substances can usually be divided into three main fractions: humic acids (HAs), fulvic acids (FAs) and humins. The division is based on their solubility. Humic and fulvic acids are soluble in aqueous solutions, whereas humins are only soluble in organic solutions. Humic acids can be separated from fulvic acids by their precipitation as a gel when the water solution of both mentioned fractions is acidified to pH approximately equal to or lower than 2. A simplified division of humic substances is shown in Figure 1 [5, 9, 10].

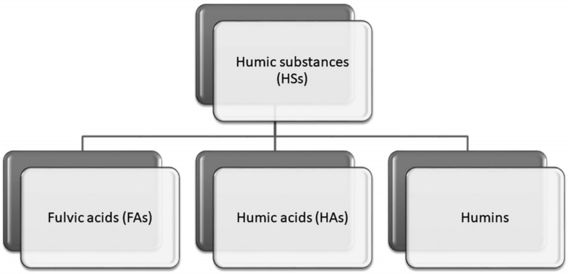

Fig. 1. The simplified division of humic substances

The structure of humic substances is not overdetermined. According to one theory, they are described as molecules consisted of polycyclic rings, often aromatic rings, which are fused or bonded to each other. Aliphatic chains and functional groups are also present in humic substances and have a significant impact on many properties of described organic compounds. It should be emphasized that the molecular structure may be different and varies depending on the humification process and environmental conditions. Figure 2 presents an example of the molecular structure model of humic acids proposed by Stevenson [4, 9–11].

The positive effect of humic substances usage on plants growth is well-known. These organic compounds can improve physical, chemical and biological properties of soil,

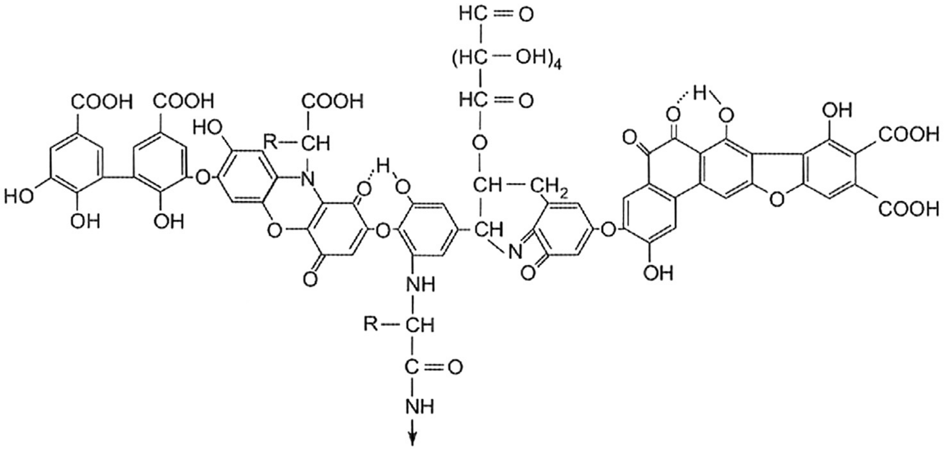

Fig. 2. The molecular structure model of humic acids proposed by Stevenson [10]

such as its sorption capacity and aeration. They also can form complexes with micronutrients, what increases availability of such fertilizing elements for plants. The addition of dark coloured humic acids determines better thermal parameters of the ground. Due to the aforementioned features, humic substances are widely applied in agriculture and horticulture. These compounds are used as soil improvers, but also as components of some sorbents [1–7, 12–16].

The obtainment of humic substances was investigated for many years. A popular method of humic and fulvic acids sourcing is their alkaline extraction from organic raw materials. Many attempts have been made to modify extraction processes such as ultrasound assisted extraction or microwave assisted extraction. It seems interesting to determine the possibility of humic acids extraction using extractants and auxiliary solutions containing fertilizer elements [17–19].

Materials and methods

The aim of this research was to determine efficiency of humic acids (HAs) extraction from peat using substances, that had fertilizer components (e.g. compounds of potassium, nitrogen, phosphorus). Due to usage of that type of extractants it was possible to receive humic substances enriched by fertilizer compounds (NPK). As carbon raw material for the extraction of humic substances with NPK peat from Zulawy region was used. Figure 3 presents schematic diagram for the technology, used for the obtaining of humic acids.

Due to the increase of humic substances availability extraction of HAs was preceded by treatment of peat with use of a mineral acid. In this process fertilizer compounds of nitrogen and phosphorus were introduced. The effect of first step of proposed technology was a change in structure of humic acids. Due to that HAs availability was higher. Depending on the adopted process solutions HNO_3, H_3PO_4, KOH, NaOH and

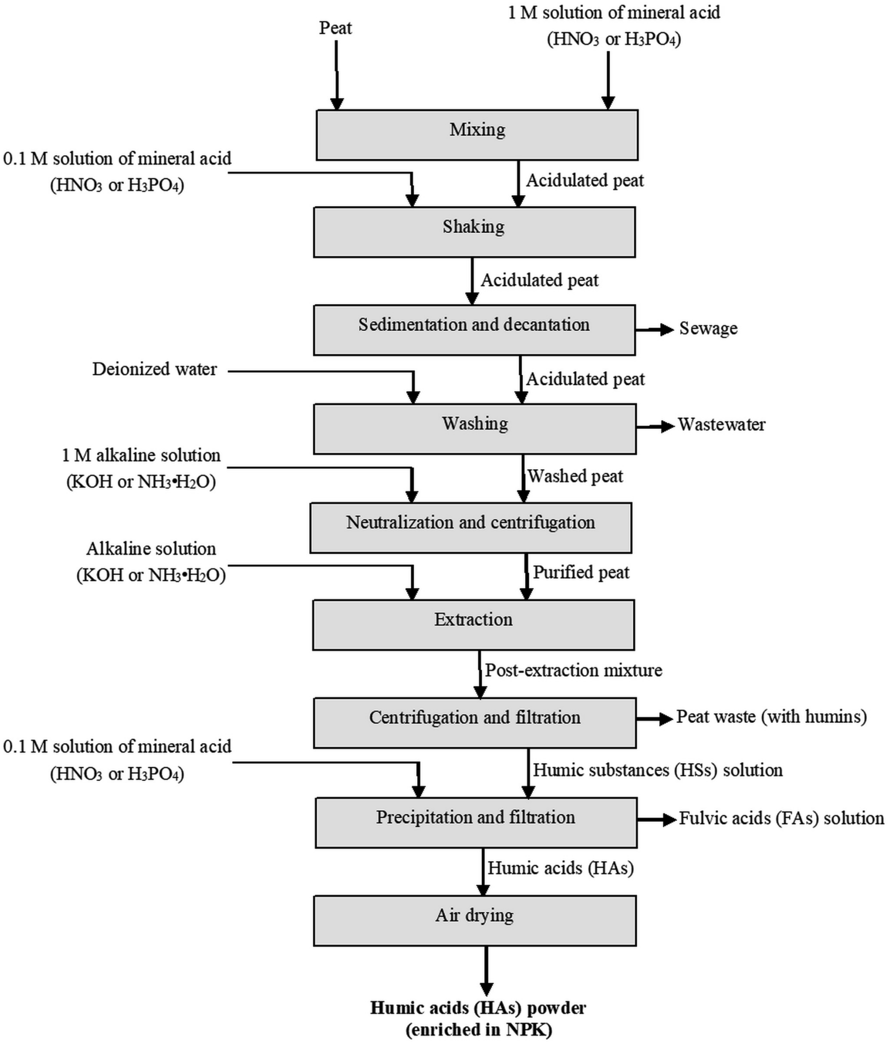

Fig. 3. Schematic diagram of the proposed technology of humic acids extraction

$NH_3 \cdot H_2O$ water solutions was used. Process solutions and used reagents are presented in Table 1.

Peat treatment with mineral acids was conducted using HNO_3 and H_3PO_4. In the process 0.1 M and 1 M acids solutions was used. Water solutions were prepared using concentrated acids (85 mass % H_3PO_4 and 65 mass % of HNO_3) from POCH S.A.

Process of carbon raw material preparing using mineral acids started with weighing 80 grams of peat into polypropylene bottles, which volume was 1 dm^3. Next raw material was mixed with 80 cm^3 of 1 M mineral acid solution (phosphoric or nitric acid). After that for each samples 720 cm^3 of 0,1 M acid solution was added. Peat

Table 1

Type of processes with used reagents for the production of humic acids with NPK

Order of inputting the substance into the process	Peat preparing by shaking with acid solution	Setting of peat pH after acid shaking	Humic acids extraction	Humic acid precipitation from extract
H_3PO_4 / KOH / $NH_3 \cdot H_2O$ / HNO_3	H_3PO_4	KOH	$NH_3 \cdot H_2O$	HNO_3
HNO_3 / NH3·H2O / KOH / H_3PO_4	HNO_3	$NH_3 \cdot H_2O$	KOH	H_3PO_4

shaking with acid solution was proceeded at room temperature for 1 hour using laboratory shaker ELPAN. After that time peat was separated form solution by sedimentation and decantation. Raw material pH was set at about 6.5 by adding of 1 M KOH or NaOH solution. After that, peat containing significant amount of liquid was centrifuged for 15 minutes at 1500 rpm. The peat prepared in this way was allowed to air dry. After 48 hours carbon raw material was transferred to a sealed container.

Main step for that technology, depending on the adopted variant of process proceeding, was implemented using 0.1 or 0.5 M solutions of KOH or $NH_3 \cdot H_2O$. The aim of that step, presented in Table 1 at column number 4, was to separate humic acids from peat.

As raw materials for humic acids obtaining were used peat samples of 25 grams for each extraction. Peat samples were inputted into 500 cm^3 conical flasks, next 375 cm^3 of extractant was added to each sample (sample to extractant mass ratio equalled 1:15). The process was carried out at 20 or 60 ^oC, in 3 series, where each of them had 15 or 45 minutes. Between the series were 15 minutes breaks. After extraction peat was separated from the extract by 15 minutes centrifugation at 3000 rpm. Next, in order to separate solid particles from the peat extract, it was vacuum filtered used qualitative hard filter paper.

To precipitate humic acids from the obtained filtrate, it was acidified using 1 M solution of nitric or phosphoric acid to the pH about 2. After that, extract was stored at 5 ^oC, until complete precipitation of humic acids.

The amount of extracted humic acids were described according to PN-G-97051- 16:1989. After humic acids precipitation, phases were separated using quantitative hard paper filter. After that, solid phase was dried at 105 ^oC for 24 hours. To determine the amount of extracted humic acids, calculated on a dry and ash-free state, dried samples were incinerated at 615 ^oC [20].

Results and discussion

The amount of extracted humic acids from carbon raw materials at given process conditions (time and temperature) is described using equation:

$$KH^{daf} = \frac{10000 \cdot (m_1 - m_2)}{m_3 \cdot (100 - W_1^a - A_1^a)} \cdot \frac{V_1}{V_2} \tag{1}$$

where: KH^{daf} is amount of extracted humic acids, calculated at dry and ash-free state [mass %]; m_1 – mass of precipitated humic acids after drying [g]; m_2 – mass of ash after sample incinerated [g]; m_3 – mass of peat sample [g]; W_1^a – moisture content in analytical peat sample [mass %]; A_1^a – ash content in analytical peat sample [mass %]. The V symbols were used for describing the volumes, respectively: V_1 – total volume of alkaline solution [cm^3]; V_2 – volume of the extract taken to precipitate humic acids [cm^3].

In Tables 1 and 2 the amount of obtained humic acids was shown, also dependencies of that parameter on temperature and extraction time for two alkaline extractants (KOH and $NH_3 \cdot H_2O$). Each experiment was done 3 times, and the average value for each points was calculated.

Table 2

The amount of extracted humic acids using $NH_3 \cdot H_2O$ as extractant, depending on the concentration of extractant, process time and temperature

Extractant concentration [$mol \cdot dm^{-3}$]	Temperature [^oC]	Series time* [min]	The amount of extracted humic acids [mass %]	Average value [mass %]
0.1	20	15	5.90 6.99 6.03	6.30
	60	45	14.12 13.16 13.61	13.63
0.5	20	15	16.39 15.14 16.53	16.02
	60	45	36.45 34.29 35.78	35.51

* Depending on the adopted variant, the process was carried out in three series of 15 or 45 minutes each, with a 15-minute break between them.

The main aim of the research was to compare the efficiency of humic acids obtaining from peat with use of different extractants, also for different temperatures and extraction times. Based on the results form Tables 2 and 3 it may be concluded, that higher efficiency of HAs obtaining was possible for more concentrated extractant. Based on comparing data in Tables 2 and 3, follows that for the same extractant concentration, conditions of temperature and extraction time, higher efficiency of humic acids obtaining from carbon raw materials was observed for KOH. The highest efficiency of HAs extraction from peat, equals 48.06 mass % was for 0.5 M solution of KOH, where process was proceeded at 3 series of 45 minutes in 60 ^oC.

Based on presented data, it can be concluded that increase of temperature, extraction time and concentration of extractant have positive effect on efficiency of humic acids obtaining in alkaline extraction process from peat. However excessive increasing of

Table 3

The amount of extracted humic acids using KOH as extractant, depending on the concentration of extractant, process time and temperature

Extractant concentration [mol · dm^{-3}]	Temperature [^{o}C]	Series time* [min]	The amount of extracted humic acids [mass %]	Average value [mass %]
0.1	20	15	19.38 17.75 20.57	19.24
	60	45	43.58 43.56 41.15	42.76
0.5	20	15	27.04 29.22 29.29	28.52
	60	45	48.75 46.83 48.59	48.06

* Depending on the adopted variant, the process was carried out in three series of 15 or 45 minutes each, with a 15-minute break between them.

temperature may have negative effect on the structure of HAs. Temperature of extraction above 80 ^{o}C may change or destroy the humic acids structure, which may results in the loss of properties related to soil structure improvement. Excessive time extension, despite the theoretical increase of efficiency of humic acids extraction may not be economically beneficial. It means that the increase of efficiency of humic acids obtaining, resulting from the extension of process time may not be high enough to compensate for the costs of running the process for a longer time.

Conclusion

Presented in that work technological solution, which aim was to connect technologies of humic acids extraction and enrichment of that substances in fertilizers components type NPK may provide production of organic fertilizer in one technological process. Moreover, replacement of traditional extractants for that process, which are chlorides and sodium compounds by fertilizer precursors for technology of HAs extraction from carbon raw materials may reduce emission of chemical compounds, that were not fully used by plants.

Replacing of HCl and NaOH, which are used in technologies of humic acids extraction from carbon raw materials, with fertilizer components (e.g. KOH, $NH_3 \cdot H_2O$, HNO_3 or H_3PO_4) allows to obtain similar efficiency than for traditional process of HAs extraction proposed by International Humic Substances Society.

Additionally, based on presented results, it is possible to determine suitability assessment of using peat form Żuławy region as carbon raw material for humic acids obtaining processes. The highest efficiency of HAs extraction for given variants was 48.06 mass %, that value has been determined in relation to the dry and ash-free product. Efficiency of HAs extraction about, 50 mass % is high, thus, the carbon raw material used in the research can be considered promising for humic acids obtaining. It is especially important due to the low calorific value of polish peat and the difficulties of its using for energy production. Using polish peat as carbon raw material for humic substances extraction processes is an interesting alternative to use of this raw material.

Proposed technology based on production of humic substances (especially humic acids) using fertilizer components. NPK components are inputted at the process of HAs extraction. Due to that it is possible to obtain soil conditioner with fertilizing properties at one technological process. Proposed technological process significantly simplifies the procedure for the production of humic substances with higher fertilization ability, which in the traditional version is based on HAs extraction and, after that process, connecting of humic acids with NPK fertilizer.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education of Poland within a frame of science subsidy for 2020 which was realized in the Department of Engineering and Technology of Chemical Processes, Wroclaw University of Science and Technology (No. 8201003902-K24W03D05).

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