ECOLOGICAL CHEMISTRY AND ENGINEERING A
Vol. 18, No. 11 2011

Krystyna HOFFMANN[1]* and Marta HUCULAK-MĄCZKA[1]

EVALUATION OF CONCENTRATION OF HUMIC SUBSTANCES IN SELECTED RAW MATERIALS AND WASTES

OCENA ZAWARTOŚCI SUBSTANCJI HUMUSOWYCH W WYBRANYCH SUROWCACH I ODPADACH

Abstract: Organic substances contained in the soil undergo a slow decomposition, as a result of it is the humus decrease. Various organic substances, especially lignite coal, are an abundant source of humus and nutrients. The main components of humus are high-molecular, amorphus humus acids. The calcium, magnesium, iron, micronutrients and some organic compounds like proteins, carbohydrates, enzymes, vitamins content are very important from the fertilizer point of view. Humus compounds are amorphus organic substances which have a various colouration from yellow to red and contain humic acids, fulvic acids, humins and bitumins. They are different in molecular weight, functional group amount, degree of polymerization and many other factors. The estimation of the possibility of lignites and hop wastes using as a source of humic acids was the aim of research. For this purpose organic carbon (by Tiurin and Alten method), fraction composition of humic acids and total organic substances, calcium and magnesium content were determined. The results of research showed the possibility of organic substances application as mineral – organic fertilizers components and the main component of humus preparations.

Keywords: organic substances, humus acids, fertilizing, lignite, hop wastes

The intense industrial development initiated in the mid-19th century resulted in improving the quality of living including not only industrial goods but also alterations in the way of feeding the population. The increasing number of people inhabiting the globe was impulse to create inventions enabling significant increase in the amount of the food and the improvement in their nutritional value. The main role in this scope fell for agricultural chemists who developed methods of obtaining the mineral fertilizers containing basic biogenic elements – phosphorus, potassium and nitrogen. Less significant, however considerable role should be assigned to alterations in the cropping practices. Together with mass applying fertilizers their adverse influence on the

[1] Institute of Inorganic Chemistry and Mineral Fertilizers, Wroclaw University of Technology, ul. M. Smoluchowskiego 25, 50–372 Wrocław, Poland, phone: +48 71 320 30 39, email: krystyna.hoffmann@pwr.wroc.pl

* Corresponding author

environment was observed. This adverse influence of fertilizer compounds on the environment can be caused by diverse factors. The most important are overdosing fertilizers ie introducing to the soil environment of large amounts of mineral fertilizers than it results from the nutrients demand of plants, the quality of the soil supporting leaching mineral elements and to a lesser degree concentration of heavy metals, resulting from applied raw materials and the method of manufacturing of mineral fertilizers. Supplying organic substance together with mineral fertilizers should be one of solutions to limit these disadvantageous processes. Among unconventional sources of organic matter a waste lignite coal of a lower energy value plays a significant role. Possibilities of using the lignite coal for fertilizer purposes result also from its peculiar physical and chemical properties as well as from big prospectivity of its applications ie possibility of supplying the horticultures with the lignite coal for years due to its huge deposits [1–3].

Properties of the lignite coal playing fundamental role in the environment and application within different fields of agriculture are [2–5]:

– the ability to absorb damp and different vapours and gasses,
– the ability of the cation exchange,
– the buffering properties,
– the concentration of organic matter.

A concentration of microelements in lignite coal, concentration of organic matter, an effect of humic acids, better availability of iron compounds which under the influence of the lignite coal are transformed into forms readily available also determine the fertilizer effect of applying organic substance [2–6].

The organic substances contained in the soil are undergoing the slow degradation because of which depletion of humus follows. Diverse organic substances, particularly lignite coal constitute the abundant source of the humus as well as nutrients. Large-molecular, amorphus humic acids are a main elements of the humus. From a fertilizer point of view a concentration of calcium, magnesium, iron, micronutrients as well as some organic compounds like proteins, carbohydrates, enzymes, vitamins is also essential. Humus compounds are amorphus organic substances of the diverse colouring, from yellow to red, containing in their composition humic and fulvic acids, humins and bitumins. They differ between themselves in the molecular weight, the number of functional groups, the degree of the polymerization, with the solubility and many different factors [4–11].

Providing the soil with organic matter is an aim of organic fertilizing and supplying plants with determined amount of nutrients, as well as counteracting adverse influences on the environment by applying mineral fertilizers. Applying organic fertilizers increase the amount of humus in the soil which is essential in proper plant nutrition. Regulating aqueous-air, sorption, red-ox and thermal relationships, as well as undervalued possibility of improving the biological activity belong to the most important functions of the organic substance performed in the soil [1, 2 ,6].

At present time of the extensive intensification of crop production utilizing potential nutrients included in organic substances is also important. Under some conditions, on account of the chemical structure, they become unavailable to plants. Natural fertilizers are an exception eg manure and litter which contain large amounts of biogenic elements like nitrogen or potassium. However a stabilization of the chemical compounds mentioned above in fertilizer constitutes a problem on due to large losses and the simultaneous environmental pollution [2–6].

Mainly peat and lignite coal belong to organic substances applied in agricultural cultivations. Sewages can also be source of organic substances under the condition of appropriate application, preparation and removing toxic and harmful for development of plants compounds. Peat and lignite coal contain nutrients from the macrogroup (calcium, phosphorus, potassium, nitrogen, magnesium, sulphur) and micronutrients (copper, zinc, iron, manganese, molybdenum, cobalt, boron), unfortunately they are unavailable to plants without preliminary chemical processing [2, 3, 12, 13].

Relationships between the crops and mineral elements were subject of examination since 19th century. In accordance with these examinations the German scientist Justus Liebig formulated a law so-called Law of the Minimum which propagates that the crop yields depend on the dose of the mineral element which in the soil appears in the smallest amount [1].

The degree of availability can be determined:

– directly – by the rate of absorption of particular compound by the root,

– indirectly – by the amount of the particular compound extracted from the soil using chemical methods.

Processes determining the availability of mineral elements by the root of the plant occur between individual phases of the soil [1].

Therefore, availability of mineral elements includes different kind of biological and chemical equilibrium processes occurring between roots and the solid, liquid and gas phase of the soil. The availability can be determined using direct method through the measurement of the amount of the compound absorbed by the root or by indirect method through the amount of the compound extracted from the soil with chemical methods applying appropriate extraction solutions. However the methods mentioned above are only an approximation describing very complicated relationships, dependent on the external factors eg climate as well as internal eg structure of the soil [1, 4, 5].

The beneficial impact on the environment is an important property of organic substances. On account of the great sorption and aqueous capacity they limit losses ensuing from the solubility of mineral elements as well as inhibit impact of the toxic substances which can pollute the soil [4, 5].

Materials and methods

The aim of conducted research was physicochemical assessment of lignite coal samples collected from Turow and Belchatow mines and so-called hop wastes, derived from hop extract production using method of the CO_2 extraction under supercritical conditions as sources of organic substance. During examinations the special attention was devoted to evaluation of concentrations of organic carbon as well as total and free humic acids.

The lignite coal is ranked among sedimentary rocks of the organic origin. It was formed at the end of the Cretaceous period. It is placed between peat and the hard bituminous coal in the rank of carbon content of primary carbonaceous material. Formation of lignite coal is a complex and complicated process, dependent on many factors ie climate, development of fauna, microorganisms, the morphology and the tectonics of given area [2–5].

A complex of amorphus humic substances is included in a lignite coal composition, where humic, hymatomelanic, fulvic acids as well as humins and bitumins can be distinguished. Considering the solubility it seems that fulvic and humic acids are of the greatest agricultural significance [10, 11].

Humic acids constitute a fraction of macromolecular compounds of the aromatic nature of the colour from dark-brown to black. It is extractable from the soil using the alkaline solvents. Their structure has not been completely identified yet. It is assumed that they are polymers, of which an aromatic core is a basic element of the structure connected with amino acids, sugars, peptides, aliphatic acids etc. The core consists of rings of the phenols type or compounds containing nitrogen in the cyclic form. Functional groups constitute the essential part of the structure of molecule. The following groups are the most important: methoxyl, carboxyl, carbonyl, phenol, quininyl, alcohol [4, 5, 10, 11].

Fulvic acids constitute a fraction of humus compounds soluble in water, NaOH solution and diluted acids. They are of yellow to yellow-brown colour. They form readily soluble salts with calcium, magnesium, sodium or potassium, however they form chelates with iron and aluminium. Their structure has not been precisely determined. It is supposed, that molecules of fulvic acid are made from benzene rings joined into the polymeric arrangement by the hydrogen bonds [2, 7, 11].

In the research on concentrations of humus substance a methodology and the laboratory analysis recommended for examinations of this type by the Soil Science Society of Poland and Polish Standards were applied [14–16].

The concentration of organic carbon in raw materials and industrial wastes can be determined using diverse methods. A Tiurin and Alten methods belong to the most investigated.

Basis of the Tiurin method [16]

The Tiurin method in the original form refers to determining concentrations of organic carbon in samples of mineral soils. However on account of resemblance of chemical composition it was applied for analyses of lignite coal samples, humus fertilizers and hop wastes. It consists in oxidizing the organic substance, using solution of potassium dichromate, contained in examined samples in the presence of the silver sulphate as catalyst. The excess of potassium dichromate is subsequently titrated using Mohr’s salt in the presence of ferroine as the indicator.

Examination procedure

Sample of the mass 0.0150 g was introduced into the conical flask of volume 250 cm^3, 0.2 g of silver sulphate and 5 cm^3 of the sulphuric acid were added. The samples prepared according to the method mentioned above were left for 1 h. After this time 40 cm^3 of potassium dichromate was added, heated up and boiled for 5 min. After cooling down approximately 50 cm^3 of the distilled water was introduced and the mixture was titrated subsequently with solution hydrated ammonium iron(II) sulphate (which titre was obtained previously using the potassium permanganate) in the presence of ferroine as the indicator.

Basis of the Alten method [14]

The Alten Method is a Tiurin analogous method which allows for determining the concentration of organic carbon in samples. The difference is that oxidizing organic carbon in the Alten method is conducted during heating samples in the water bath for 3 h.

Examination procedure

Weighed portion of the sample in the amount of 0.0150 g was introduced into the 100 cm^3 calibrated flask. 10 cm^3 of solution potassium dichromate and 16 cm^3 of the concentrated sulphuric acid were added. The flasks prepared according to the method mentioned above were put in the warm water bath and heated for 3 h. After cooling, flasks were filled up with the distilled water. Then 25 cm^3 of solution was transferred into the conical flask and titrated with Mohr's salt in the presence of phenylantranile acid to the change of the colour to dark brown.

Method for determining humus [5]

The method of determining humus in organic materials consists in analyzing the content of organic carbon in samples and subsequent multiplying the result by value of the rate equal 1.724.

$$\% \text{ humus} = \text{concentration } C_{org} \, [\%] \cdot 1.724$$

Method for determining fractional composition of organic matter using Tiurin method [14]

The method refers to determining of fractional composition of humus in soils. On account of the subject of the research it was used for analyses of tested organic materials. This method enables to extract and determine among others sodium humates, humic and fulvic acids.

Comparison of results of the organic carbon concentrations for every fraction of examined samples are demonstrated in Table 1.

Table 1

Fractional composition of samples determined by Tiurin method (C_{org} [%]) [Fraction no. 2 – 0.5 M Na_2SO_4; Fraction no. 3 – 0.1–0.02 M NaOH after decalcination; Fraction no. 4a – 0.25 M and 0.5 M H_2SO_4; Fraction no. 4b – 0.1–0.02 M NaOH alternated with acid; Fraction no. 5 – post-extraction residue; Fraction no. 6 – directly 0.25M H_2SO_4; Fraction no. 7 – directly 0.1 M NaOH]

Groups and fractions	Fractions marking	Turow lignite coal	Belchatow earthy lignite coal	Commercial humus fertilizer	Hop wastes
Substances extracted with Na_2SO_4	2	6.420	4.088	14.016	2.920
Humic acids fractions	7	2.37	4.09	2.92	1.17
	3–7	7.59	4.92	11.68	9.87
	4b	15.77	18.69	22.19	14.30
	Total	25.73	27.70	36.79	25.34
Fulvic acids fractions	6–2	2.34	5.26	4.67	4.67
	7	1.75	1.17	4.09	2.92
	3–7	4.67	2.92	8.76	5.84
	4b	2.92	1.75	5.26	2.34
	Total	11.68	11.10	22.78	15.77
Substances hydrolyzed in H_2SO_4	4a	3.21	2.57	3.80	2.45
Humates	5	53.14	47.89	61.32	42.05

The comparison of organic carbon concentrations in examined samples, applying the Tiurin or Alten method, respectively is presented in Fig. 1. Any significant differences were not stated. The results of concentrations of organic carbon for both methods were comparable.

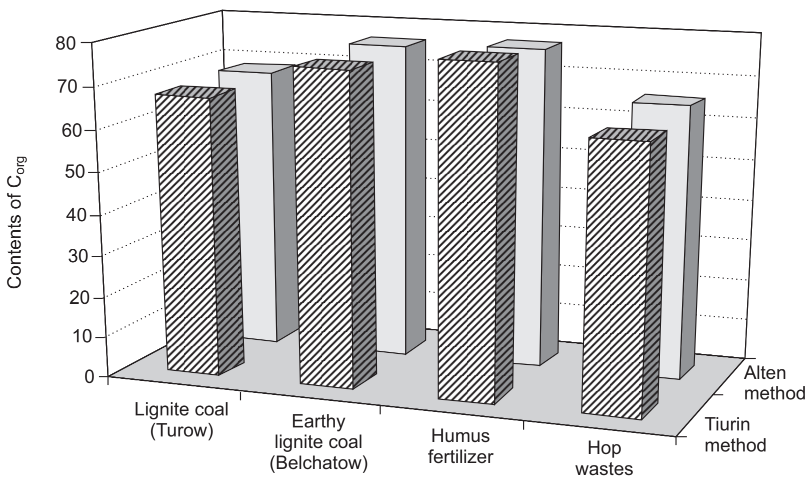

Fig. 1. Comparison of concentration of C_{org} in selected samples evaluated by Tiurin and Alten method

Total humic acids include the humic acids presented in the free form and the ones which are bound into salt forms. They are obtained by the extraction with alkaline solution of sodium pyrophosphate and secondary extraction with sodium hydroxide. Humic acids can be subsequently precipitated from the solution by treating them with mineral acids eg HCl.

Free humic acids are humic acids extracted from organic matter which appear as a result of treating the lignite coal or different organic raw material with sodium hydroxide, and then with mineral acids in order to precipitate them from the solution.

Comparison of concentrations of total and free humic acids contained in lignite coal, humus fertilizers and hop wastes is presented in Table 2.

Table 2

Concentration of total and free humic acids in examined samples

Sample / Concentration of humic acids	Lignite coal (Turow)	Earthy lignite coal (Bełchatów)	Humus fertilizer	Hop wastes
Concentration of total humic acids [% mas.]	43.16	53.35	47.17	27.16
Concentration of free humic acids [% mas.]	23.76	26.80	24.69	23.89

Concentration of total *humic acids* – $(HA)_{tB}^{daf}$ in examined samples calculated for dry and ash-less state; as well as free humic acids $(HA)_{fB}^{daf}$ of organic matter calculated for dry and ash-less state were calculated in % mas. according to the following formula:

$$(HA)_{tB}^{daf} = \frac{10000 \cdot (m_4 - m_5)}{m_6 (100 - W_1^a)} \cdot \frac{V_0}{V_1},$$

where: m_4 – mass of total humic acids [g],
m_5 – mass of residue after incineration of total humic acids [g],
m_6 – mass of weighed amount of sample [g],
V_0 – total volume of the alkaline solution [cm^3],
V_1 – volume of the solution collected for examination of total humic acids [cm^3],
W_1^a – humidity content in the sample [% mas.].

$$(HA)_{fB}^{daf} = \frac{10000 \cdot (m_7 - m_8)}{m_6 (100 - W_1^a)} \cdot \frac{V_0}{V_1},$$

where: m_7 – mass of free humic acids [g],
m_8 – mass of residue after incineration of humic acids [g],
m_6 – mass of weighed amount of sample [g],
V_0 – total volume of the free humic acids [cm^3],
V_1 – volume of the solution collected for examination [cm^3].

Conclusions

It results from examinations carried out that examined substances are characterized by high concentration of organic carbon and they can constitute the valuable component in mineral-organic fertilizers applicable for improving the physicochemical properties of soils and for eco-friendly purposes consisting in suppressing uptake of intoxicants. High concentrations of total and free humic acids and fractional composition characterizing concentrations of fulvic acids, completely water-soluble and of humic acids soluble in the alkaline environment indicates the possibility of inventing mineral--organic preparations for plant fertilizing purposes containing both micro as well as macronutrients.

References

[1] Fotyma M. and Mercik S.: Chemia rolna, PWN, Warszawa 1995.
[2] Maciejewska A.: Węgiel brunatny jako źródło substancji organicznej i jego wpływ na właściwości gleb, Ofic. Wyd. Polit. Warszawskiej, Warszawa 1998.
[3] Maciejewska A.: *Ekologiczne aspekty nawozu organiczno-mineralnego wytworzonego z węgla brunatnego*, Zesz. Probl. Nauk Roln. 1993, **411**, 311–318.
[4] Bednarek R., Dziadowiec H., Pokojska U. and Prusinkiewicz Z.: Badania ekologiczno-gleboznawcze, Wyd. Nauk. PWN, Warszawa 2004.
[5] Drozd J., Licznar M., Licznar S., Weber J.: Gleboznawstwo z elementami mineralogii i petrografii, Wyd. AR we Wrocławiu, Wrocław 1997.
[6] Górecki H., Hoffmann K., Hoffmann J. and Szynklarz B.: *Badania nad wpływem dodatku węgla brunatnego na poprawę właściwości fizykochemicznych gleby i podłoży*, Chem. Inż. Ekol. 2000, **7**(5), 439–445.
[7] Kalembasa S. and Fengler S.: Wykorzystanie węgla brunatnego w nawożeniu, Wyd. Wyż. Szk. Pedagog. Siedlce 1992.
[8] Roga B.: Kopalne paliwa stałe, Wyd. Geolog., Warszawa 1958.
[9] Janos P. and Kozler J.: *Thermal stability of humic acids and some of their derivatives*, Fuel 1995, **74**(5), 708–713.
[10] Beckett R.: *Determination of molecular weight distributions of fulvic and humic acids using flow field-flow fraction*, Environ. Sci. Technol. 1987, **21**, 289–295.
[11] Gonet S.: *Struktura substancji humusowych*, Zesz. Probl. Post. Nauk Roln. 1993, **411**, 184–194.
[12] Hoffmann K., Hoffmann J. and Lewandowska B.: *The guano bats – studies on the fertilizer application*, Polish J. Chem. Technol. 2004, **6**(4), 22–25.
[13] Hoffmann K. and Hoffmann J.: *The utilization of peat, lignite and industrial wastes in the production of mineral-organic fertilizers*, Amer. J. Agric. Biol. Sci. 2007, **2**(4), 254–259.
[14] Dziadowiec H. and Gonet S.: Przewodnik metodyczny do badań materii organicznej gleb, Polskie Towarzystwo Gleboznawcze, Warszawa 1999.
[15] PN-G-97051-16:1989, Oznaczanie wydajności ekstraktu toluenowego (bituminów), zawartości żywic w ekstrakcie oraz zawartości kwasów huminowych w węglu brunatnym.
[16] Polska Norma PN-Z-15011-3:2001, Oznaczanie zawartości węgla organicznego.

OCENA ZAWARTOŚCI SUBSTANCJI HUMUSOWYCH W WYBRANYCH SUROWCACH I ODPADACH

Instytut Technologii Nieorganicznej i Nawozów Mineralnych
Politechnika Wrocławska

Abstrakt: Celem prowadzonych prac badawczych była ocena możliwości wykorzystania, jako źródła kwasów huminowych, krajowych węgli brunatnych i wychmielin z przemysłu browarniczego. W ramach analiz oznaczono C_{org} metodą Tiurina i Altena, składy frakcyjne kwasów huminowych, ogólną zawartość substancji organicznej, zawartość wapnia oraz magnezu. Wyniki badań wskazują na możliwość zastosowania badanych substancji organicznych jako komponentów nawozów mineralno-organicznych i głównego składnika preparatów humusowych.

Słowa kluczowe: substancja organiczna, kwasy humusowe, nawożenie, węgiel brunatny, wychmieliny