

Fertilizers with Humic Substances - Some Characteristics

CARMEN SIRBU^{1*}, TRAIAN MIHAI CIOROIANU¹, LAVINIA PARVAN¹, ADRIANA GRIGORE¹, DUMITRITA IOANA VASILE²

¹National Research-Development Institute for Soil Science, Agrochemistry and Environment Protection, Bucharest, 61Marasti. Blv., 011464, Bucharest, Romania

²University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 2-14 Regina Elisabeta Blv., 030018, Bucharest, Romania

Using as fertilizers the substances containing humic compounds proved to be effective in a wide range of cultures and applied to different types of soil. The types and number of fertilizers that are composed of organic substances of plant origin are very numerous due to the variation of sources from which they can be obtained. The range of fertilizers containing humic substances as source of plant origin has extensively developed both due to the sources from which they can be obtained and to the mode of extraction (separation) from them. Such extracts can be used as such or combined with other organic or mineral substances, and this possibility leads to obtaining one of the largest classes of fertilizers, known as organo-mineral fertilizers. This paper presents a technology for obtaining complex fertilizers with humic substances, as well as the physicochemical and agrochemical characteristics of two fertilizers experimentally obtained.

Keywords: fertilizers, humic substances, foliar fertilization, lignite

Humic substances are a group of organic substances with common physicochemical characteristics (soluble in NH_4OH or NaOH , with HCl solution precipitated) and a complex and heterogeneous structure of the compounds [1,2,7].

Humic substances contain, apart from higher or lower fragments of lignin, proteins and sugars, a number of hydroxyl compounds, aromatic poly-carboxylic acids, quinones, heterocycles with N and O, amino-acids [8]. Structural units are connected between them by various types of links: -O-, -NH-, -N=, -CH₂-, -S-S- and chains of carbon atoms of different lengths [5-7].

There is a positive relation between the content of humic substances in the soil or applied through fertilization and the yield and quality of agricultural production, due to: the increased efficiency of conventional fertilizers and plants metabolism, stimulating seeds germination and plant root development, increasing the chlorophyll content and the yield of RNA and ATP, improving the soil capacity to retain water in soil and an improved pH, increasing the resistance to the factors of climatic and technological stress [3,4].

The positive role of humic material in agriculture has been widely accepted over the past decades; nitrogen-rich extracts act as fertilizers and growth stimulators [9,10].

Experimental part

Materials and method

The processes of extraction and separation of humic substances in order to obtain organic-mineral fertilizers took into account the physico-chemical properties of humic and fulvic acids in alkaline medium of reaction, respectively in acid medium of reaction, as well as their determination in the matrix of NPK type [4].

Experiments conducted in the laboratory stage were performed on a coal mass in the category of lignite (Rovinari, Motru, Matasari) using as alkali for the extraction of humic and fulvic substances K_2CO_3 and KOH , knowing that the greatest amount extracted is obtained in alkaline medium [7].

The processes of extraction and separation took into account the physical and chemical properties of humic and fulvic acids in an alkaline medium of reaction, respectively in acids medium of reaction [5-7,9].

In order to determine the curves of extraction of humic substances (AH) from lignite, basic potassium solutions have been used (K_2CO_3 in fig. 1 and KOH in fig. 2) for concentration of K_2O : 0.5% K_2O ; 0.75% K_2O ; 1.0% K_2O ; 5.0% K_2O and 10.0% K_2O (figs. 1-4).

Figures 1 and 2 show that the largest amount of humic acids extracted was obtained when the KOH solution was used. Also, from figures 1-4 it can be seen as the best

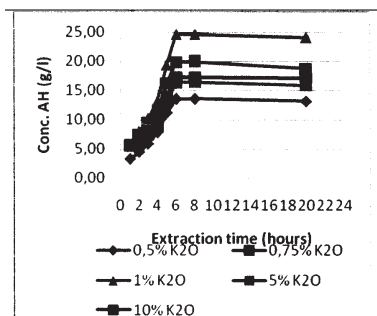


Fig. 1. Evolution of the amount of humic acid extracted depending on the alkali concentration (K_2CO_3), respectively 0.5% K_2O (1); 0.75% K_2O (2); 1% K_2O (3); 5% K_2O (4) and 10% K_2O (5) and different times

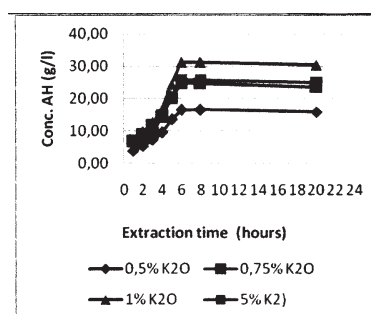


Fig. 2. Evolution of the amount of humic acid extracted depending on the alkali concentration (KOH), respectively 0.5% K_2O (1); 0.75% K_2O (2); 1% K_2O (3); 5% K_2O (4) and 10% K_2O (5) and different times

* email: carmene.sirbu@yahoo.ro

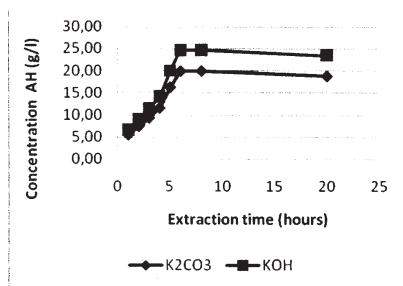


Fig. 3 Evolution of the amount of humic acids extracted depending on the nature of the alkali (K_2CO_3 respectively KOH) for a concentration of 0.75% K_2O and different times

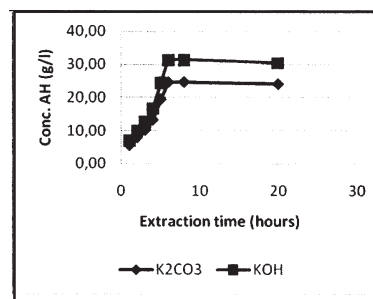


Fig. 4 Evolution of the amount of humic acids extracted depending on the nature of the alkali (K_2CO_3 respectively KOH) for a concentration of 1% K_2O and different times

extraction yield of humic acids was obtained for a concentration of 0.75% of alkaline solution. One reason for this could be the difference for values of pH and ionic strength solution of the solution even at the same concentration in K_2O [11-15].

Both raw materials, coal mass (lignite) and humic acids extracted in the laboratory were characterized through differential thermal analysis [4]. Samples of lignite and humic substances, intermediates in the process of obtaining organic and mineral fertilizers, were thermogravimetrically analyzed in the temperature ranging: ambient temperature – 800°C, in air flow, with heating rate of 10°C/min, tracing simultaneously TG curves – thermogravimetric analysis, DTG – mass derivative in relation to time, DTA – thermal differential analysis and DSC – calorimetric analysis.

For the determination of the NPK fertilizers with humic substances experiments in laboratory were performed on a stainless steel installation coupled to an ultra-thermostat with the possibility of recycling the heating/cooling agent, regulating and keeping the reaction temperatures in the range 0 – 100°C. Mixing of reactants was carried out with an electronic laboratory mixer, with the possibility of controlling the stirring speed up to 3000 rpm.

Results and discussions

Samples of lignite and humic substances, intermediated in the process of obtaining organic-mineral fertilizers were thermo-gravimetrically analyzed in the temperature ranging: ambient temperature ÷ 800°C, in air flow, with heating rate of 10°C/min. Results are shown in the figures 5 – 7.

By examining the thermograms of the two samples there are similarities when they were heated in air flow. In the first stage of the decomposition process,

TG curve area until to a temperature of 125-130°C, is recorded drying stage, followed by loss of volatiles step up to temperature of 340-350°C.

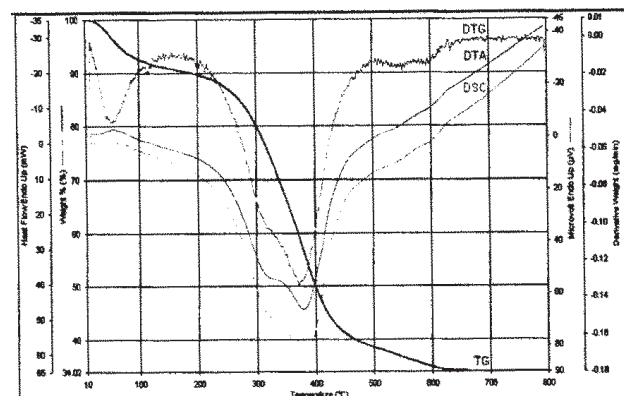


Fig. 5. Thermogram of the lignite sample from the Rovinari mine

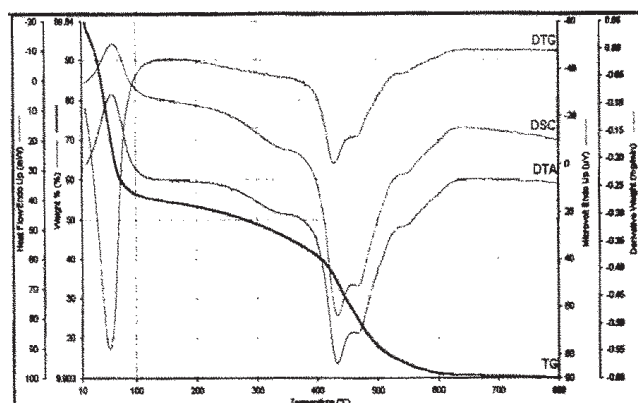


Fig. 6. Thermogram of the sample of humic acids extracted from lignite from the Rovinari mine

Oxidative degradation of organic matter remaining after removal of volatiles, begins at 340 °C and continues up to about 500 °C. This step is strongly exothermic and has the maximum of the DTG curve at 380-410 °C and for the curves DTA and DSC at 486 and 416°C. Final weight losses are 66% for coal and 91% for the sample of humic substances.

N°.	Physicochemical characteristics	Experimental fertilizers Concentrations (g/l)	
		HUMIC V1	HUMIC V2
1	Nitrogen, N total, min	150	170
2	Phosphorus, P_2O_5 , min	30	35
3	Potassium K_2O min	35	40
4	Iron, Fe, min	0.4	0.4
5	Copper, Cu, min	0.15	0.2
6	Zinc, Zn, min	0.12	0.2
7	Magnesium, Mg, min	0.3	0.4
8	Manganese, Mn, min	0.2	0.4
9	Boron, B, min	0.3	0.2
10	Sulphur, SO_3 , min	20	25
11	Organic substances, including:	25	30
	humic compounds, min	10	15
12	pH, units of pH	6.65	6.75
13	Density, g/cm^3 , min	1.22	1.23

Table 1
EXPERIMENTAL FERTILIZERS –
PHYSICO-CHEMICAL CHARACTERISTICS

Version N°.	Treatment	Number of treatments	Quantity of solution litres/ha	Quantity of NPK fertilizers and others kg/ha	Production of seeds (kg/ha)	Increase	
						kg/ha	%
1	Witness/Control	-	-	-	2123	-	100,0
2	HUMIC V1	1	300	92.0	2870	747	135.2
3	HUMIC V2	1	300	110.2	2900	777	136.6

Table 2
EFFICIENCY OF EXPERIMENTAL FERTILIZERS WITH RADICULAR APPLICATION TO SUNFLOWER, GROWN ON CAMBICCHEROZEM

Version N°.	Treatment	Number of treatments	Solution concentration %	Quantity of fertilizers used litres /ha		Production of seeds (kg/ha)	Increase		
				To one treatment	To all treatments		kg/ha	%	kg/litre fertilizer
1	Witness/Control	-	-	-	-	4360	-	100.0	-
2	HUMIC V1	2	0.5	2.5	5.0	4790	430	109.8	86.0
3	HUMIC V2	2	0.5	2.5	5.0	4860	500	111.5	100.0

Table 3
EFFICIENCY OF EXPERIMENTAL FERTILIZERS WITH FOLIAR APPLICATION TO RAPE, GROWN ON CAMBICCHEROZEM

One of the undesirable features of alkali extraction is that this dissolve silica from the mineral matter and this silica contaminates the organic fractions separated from de raw materials [7].

The compositional range for the 2 formulas of experimental fertilizers, determined as a result of the research activities carried out in the laboratory stage, are shown in the table 1.

Experimentally, there were obtained samples from each version of NPK fertilizer with humic substances that have been characterized and applied by incorporation in soil and respectively extra-radicular, in experimental field, at S.C. AGROFARM HOLDING S.R.L. Fetesti, on the crops of winter wheat and rape, as well as in the National Network for Fertilizers Testing on the crops of wheat, corn, sunflower and rape, in order to be authorized for use in agriculture.

Agrochemical testing was conducted within single factor experiments, arranged in four repetitions, by foliar application and in soil compared to unfertilized witness. Some of the results obtained are presented in tables 2 and 3.

Means were compared by using Student test at the level of significance $\alpha = 0.05$.

According to the data in tables 2 and 3 it can be seen that there are significant differences for the two fertilizers compared to control and these are statistically insured.

Researches were carried out under the project PCCA Type 2, Financing Contract N°.109/2012 UEFISCDI "Regeneration of soil fertility and increasing yields by using new fertilizer with natural organic substances" (HUMIFERT).

Conclusions

It was developed a method of extracting humic substances from the coalmass, lignite, using a potassium alkali.

It was developed a technology for obtaining complex fertilizing structures of the type NPK, with mesoelements, microelements and humic substances.

Raw materials, extracted humic substances and fertilizers have been complexly characterized physically and chemically, as well as by using technique thermogravimetry.

There were obtained samples of fertilizers with humic substances that have been agro-chemically tested, applied both by soil incorporation and by extra-radicular method.

The fertilizers with foliar or radicular application provided production increases between 10 and 38% compared to controls.

References

- CHIRIAC, J., BARCA, F., Comparative Study of Humic Acid Extract with Ammoniacal Solutions from Coals in Inferior Rank and from Romanian Soil, Rev. Chim. (Bucharest), **60**, no. 4, 2009, p. 432
- ZOJA, V. L. G., BARBORA, A., MILOSLAV, P., JIRI, K., Lignite pre-treatment and its effect on bio-stimulative properties of respective lignite humic acids, Soil Biology & Biochemistry, **41**, 2009, p.1894
- ALI, V. K., HAKAN, Ç., MURAT, A. T., BARIS, B. A., Effects of soil and foliar applications of humic substances on dry weight and mineral nutrients uptake of wheat under calcareous soil conditions, Australian Journal of Basic and Applied Sciences, **3**, 2009, p. 1266
- ŞIRBU, C., CIOROIANU, T., ROTARU, P., About the humic acids and thermal behaviour of some humic acids, Annals of the Faculty of Physics in Craiova, **20**, 2009, p. 126
- TIPPING, E., Cation binding by humic substances, **12**, 2002, p. 42
- KIM, H. T., Humic matter in soil and the environment, 2003, p. 290
- STEVENSON, F.J., Humus Chemistry, 1994, p. 40
- SAMIOS, S., LEKKAS, T., NIKOLAOU, A., GOLFINOPOULOS, S., Structural investigations of aquatic humic substances from different watersheds, Desalination, 2007. p. 210
- SCHNITZER, M., KHAN, S.U., Humic substances in the environment. Marcel Dekker Inc., New York, 1972
- CHASSAPIS, K., ROULIA, M., TSIRIGOTI, D., Chemistry of metal-humic complexes contained in Megalopolis lignite and potential application in modern organomineral fertilization, International Journal of Coal Geology, **78**, 2009, p.288
- ZHOU, P., YAN, H., GU, B., Competitive complexation of metal ions with humic substances, Chemosphere, **58**, 2005, p.1327
- PLAZA, C., SENES, I N., GARCÍA-GIL, J.C., POLO, A., Copper (II) complexation by humic and fulvic acids, from pig slurry and amended and non-amended soils, Chemosphere, **61**, 2005, p.711
- GONDAR, D., IGLESIAS, A., LO´PEZ, R., FIOL, S., ANTELO, J. M., FLORENCIO A., Chemosphere Copper binding by peat fulvic and humic acids extracted from two horizons of an ombrotrophic peat bog, **63**, 2006, p.82
- FURUKAWA, K., TAKAHASHI, Y., Effect of complexation with humic substances on diffusion of metal ions in water, Chemosphere, **73**, 2008, p.1272
- ZACCONE, C., SOLER-ROVIRA, P., PLAZA, C., COCOZZAA, C., MIANO, T.M., Variability in As, Ca, Cr, K, Mn, Sr, and Ti concentrations among humic acids isolated from peat using NaOH, Na₄P₂O₇ and NaOH+Na₄P₂O₇ solutions, Journal of Hazardous Materials, **167**, 2009, p. 987

Manuscript received: 29.09.2014