

## FERTILIZERS WITH HUMIC SUBSTANCES - DEVELOPMENT AND CHARACTERIZATION OF NEW PRODUCTS

Carmen SÎRBU<sup>1</sup>, Traian CIOROIANU<sup>1</sup>, Geanina BIREESCU<sup>2</sup>, Adriana GRIGORE, Ana-Maria STĂNESCU<sup>1</sup>, Bogdan RUJOI<sup>1</sup>, Lavinia BURTAN<sup>1</sup>, Nicoleta MĂRIN<sup>1</sup>, Daniela MIHALACHE<sup>1</sup>, Mariana IANCU<sup>1</sup>, Monica DUMITRAȘCU<sup>1</sup>, Emilia NICU<sup>3</sup>

e-mail: carmene.sirbu@yahoo.ro

### Abstract

Fertilizers with humic substances can be used on different types of soil, as well as in technologies for improving degraded or contaminated soils and they proved effective on a wide range of cultures. Due to the variety of sources from which they can be obtained, there are many types of fertilizers containing natural biostimulating substances. This paper presents the development of a range of complex NPK liquid fertilizers with humic substances, meso and micronutrients. The extraction processes, the humic substances separation, and the organo-mineral fertilizers technology were conducted regarding the physicochemical properties of the humic and fulvic acids in the alkaline/acidic reaction media, as well as their stability in the NPK, meso and micronutrients matrix. Two of the experimental fertilizers are physicochemically characterized and their agrochemical efficiency is shown by the results obtained in the National Fertilizers Testing Network. In the case of soil incorporation of the experimental fertilizers, the average yield increases, as compared to the unfertilized control, were ranging from 37.8% for sunflower crop to 42.3% for sugar beet crop.

**Key words:** humic substances, organic-mineral fertilizers, fertilization.

In the last period the diversification of organo-mineral fertilizers has experienced an explosive growth due to new fertilizing technologies used in agriculture. But when applying these new fertilizing formulas, there must be respected the requirements imposed by the European environmental legislation and also, take into account the needs of a sustainable agriculture.

Worldwide studies conducted on fertilizers with humic substances have shown that there is a positive relation between the content of humic substances in the soil or that applied through fertilization and the yield and quality of crops due to: increasing the efficiency of the conventional fertilizers, stimulating germination of seeds, root development and plant metabolism, increasing the activity of photosynthesis, improving the soil's capacity to retain water, increasing resistance to climatic and technological stress factors (Ali V.K. *et al*, 2009; Chassapis K. *et al*, 2009; Delgado A. *et al*, 2002; Schnitzer M., Khan S.U., 1972; Sirbu C. *et al*, 2009; Sirbu C. *et al*, 2010; Zoja V.L.G. *et al*, 2009).

Fertilizers with humic substances can be used on different types of soil and proved to be

effective on a wide range of cultures. The range of fertilizers containing humic substances is so diversified due to the numerous sources from which they can be obtained, different processes of extraction and separation of the active compounds, and also their technology of application (Furukawa K. *et al*, 2008; Gondar D. *et al*, 2006; Plaza C. *et al*, 2005; Sirbu C. *et al*, 2010; Sirbu C. *et al*, 2015; Zaccone C. *et al*, 2009; Zhou P. *et al*, 2005).

### MATERIAL AND METHOD

Elaboration of the technology for extracting humic substances and for humic acid separation was carried out using lignite from Rovinari mining. The coal mass has a content of 60% organic matter and 25% humic substances.

The extraction of humic substances from the mass of lignite was conducted in an alkaline - oxidant media - by the use of nitric acid and the injection of air into the reaction mass.

The yield of the extraction of humic substances depends on many factors among which can be mentioned: concentration of the solution extraction, lignite - extraction solution ratio, temperature and time of extraction (Kim H.T. 2003; Schnitzer M., Khan S.U., 1972; Stevenson F.J.,

<sup>1</sup> National Research and Development Institute for Soil Science, Agro-chemistry and Environment, Bucharest

<sup>2</sup> Institute of Biological Research, Iasi

<sup>3</sup> University of Agronomic Sciences and Veterinary Medicine, Bucharest

1994; Tipping E., 2002). In order to find the optimum extraction time, were made determinations of the humic acids concentration from the solution at different stages of extraction. Also, there were used extraction solutions with different concentrations of  $K_2O$ .

Based on the analysis of the experimental data resulted that higher concentrations of humic acids were obtained when using alkaline extraction solutions with a concentration of 0.75%  $K_2O$  and 1.0%  $K_2O$ .

The extraction processes, the humic substances separation, and the organo-mineral fertilizers technology were conducted regarding the physico-chemical properties of the humic and fulvic acids in the alkaline/acidic reaction media, as well as their stability in the NPK, meso and micronutrients matrix (Chassapis K. *et al*, 2009; Chiriac J., Barca T, 2009; Furukawa K. *et al*, 2008; Gondar D. *et al*, 2006; Plaza C. *et al*, 2005; Stevenson F.J., 1994; Zaccone C. *et al*, 2009; Zhou P. *et al*, 2005; Zoja V.L.G. *et al*, 2009).

The new organic-mineral fertilizers have complex synergistic structures of mineral nutrients and bioactive natural compounds (humic and fulvic acids). Using a micro-installation were made numerous experiments for determining the optimum technological process to obtain the lab-scale fertilizer variants.

Following the elaboration and validation of the technology for extracting humic substances and developing new organic-mineral fertilizers there were manufactured two batches of 1,000 liters. The fertilizers were physicochemically characterized and tested in the National Fertilizers Testing Network in order to determine their efficiency and authorise their use in Romanian agriculture.

## RESULTS AND DISCUSSIONS

The physicochemical characteristics of the fertilizers samples obtained during the development and validation of the technology at lab scale are presented as follows ( $g/cm^3$ ):

**HUMIFERT:** Total nitrogen, N - 154; Phosphorus,  $P_2O_5$  - 32; Potassium  $K_2O$  - 37; Iron,

Fe - 0.39; Copper, Cu - 0.16; Zinc, Zn - 0.11; Magnesium, Mg - 0.29; Manganese, Mn - 0.21; Boron, B - 0.31; Sulfur,  $SO_3$  - 18.6; Organic substances - 27; Humic substances - 8,8; Density - 1.18.

**HUMIFERT PLUS:** Total nitrogen, N - 172; Phosphorus,  $P_2O_5$  - 35; Potassium  $K_2O$  - 41; Iron, Fe - 0.44; Copper, Cu - 0.22; Zinc, Zn - 0.21; Magnesium, Mg - 0.31; Manganese, Mn - 0.21; Boron, B - 0.32; Sulfur,  $SO_3$  - 25; Organic substances - 32; Humic substances - 13; Density - 1.18

The agrochemical testing of the fertilizers was performed in the National Network for Fertilizers Testing in order to obtain the authorization/license and RO-ÎNGRĂȘĂMÂNT label for agriculture use and distribution in Romania in accordance with 6/22/2004 Order.

The agrochemical experiments carried out using the humic substances fertilizers were conducted as single factorial experiments by soil incorporation application (and compared to a unfertilized control sample), arranged in randomized experimental variants, using four replicates and unfertilized soil.

The experimental investigations conducted in the National Network for Fertilizers Testing were held at the USAMV Didactic and Experimental Station and Ezăreni- Iasi field farm.

The energetic efficiency (Mcal/ha), represents an indicator of the production increase and was calculated by means of the specific methodology (Teșu I., Baghinschi V., 1984).

The main quality and fertility characteristics of the soil (cambic chernozem) are given in Table 1.

The productive and energetic efficiencies of the fertilizers investigated in this study, applied by soil incorporation in dosages of 200 liters/ha are summarized in Tables 2 ÷ 4.

Table 1

Main physical, chemical and biological properties of the soil resources

Property	Depth (cm)	Value
Soil texture (%coloidal clay)	0-20	35.70- 36.9
Aeration porosity (PA%)	0-20	15 - 20
Soil reaction (pH $H_2O$ )	0-20	6.83 – 7.22
Humus (%)	0-20	3.37 – 3.58
Total nitrogen content Nt (%)	0-20	0.19 – 0.23
Mobile phosphorus content (ppm)	0-20	63 – 73
Mobile potassium content (ppm)	0-20	223 - 264
Degree of base saturation, V (%)	0-20	87 - 92
Soil respiration (mg $CO_2$ )	0-20	28.32 – 40.01
Dehydrogenase (mg TPF)	0-20	18.52 – 20.13



for the sunflower crop, respectively 40.8 and 42.3% for the sugar beet crop. For all the analyzed crops, the outcome energy indicators (OUTPUT and energy balance) show higher values than those of INPUT, resulting thus significant increases as concerns the energy and the products (crops) as a result of using the humic substances fertilizers.

### ACKNOWLEDGMENTS

Researches were carried out under the project PCCA Type 2, Financing Contract No.109/2012 UEFISCDI "Regeneration of soil fertility and increasing yields by using new fertilizer with natural organic substances" (HUMIFERT).

### REFERENCES

- Ali V. K., Hakan Ç., Murat A. T., Baris B. A., 2009 - *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, 3:1266.
- Chassapis K., Roulia M., Tsirigoti D., 2009 - *Chemistry of metal-humic complexes contained in Megalopolis lignite and potential application in modern organomineral fertilization*, International Journal of Coal Geology, 78:288.
- Chiriac J., Barca F., 2009 - *Comparative Study of Humic Acid Extract with Ammoniacal Solutions from Coals in Inferior Rank and from Romanian Soil*, Rev. Chim. (Bucharest), 60:32.
- Delgado A., Madrid A., Kassem S., Andreu L., Del Campillo M. C., 2002 - *Phosphorus fertilizer recovery from calcareous soils amended with humic and fulvic acids*, Plant and Soil 245: 277–286.
- Furukawa K., Takahashi Y., 2008 - *Effect of complexation with humic substances on diffusion of metal ions in water*, Chemosphere, 73: 1272.
- Gondar D., Iglesias A., Lo'Pez R., Fiol S., Antelo J. M., Florencio A., 2006 - *Copper binding by peat fulvic and humic acids extracted from two horizons of an ombrotrophic peat bog*, Chemosphere, 63:82.
- Kim H. T., 2003 - *Humic matter in soil and the environment*, 290.
- Plaza C., Senes I N., Garcia-Gil J.C., Polo A., 2005 - *Copper (II) complexation by humic and fulvic acids, from pig slurry and amended and non-amended soils*, Chemosphere, 61:711.
- Schnitzer M., Khan S.U., 1972, *Humic substances in the environment*. Marcel Dekker Inc., New York
- Sîrbu C., Cioroianu T., Rotaru P., 2009 - *About the humic acids and thermal behaviour of some humic acids*, Annals of the Faculty of Physics in Craiova, 20:126.
- Sîrbu C., Cioroianu T., Pohrib C., Lazar R., Dumitrascu M., 2010 - *Development of new organo-mineral fertilizer use in sustainable agriculture*, Simpozionul stiintific anual cu participare internationala, "Agricultura ecologica - prioritati si perspective", Lucrari stiintifice USAMV Iasi, seria Agronomie, 52.
- Sîrbu C., Cioroianu T., Rotaru P., 2010 - *About the humic acids and thermal behaviour of some humic acids*, Analele Facultatii de Fizica din Craiova, 20:120-126.
- Sîrbu C., Cioroianu T., Parvan L., Grigore A., Vasile D. I., 2015 - *Complex fertilizers with humic substances physicochemical and agrochemical characteristics*, Revista de Chimie, 66: 1061-1063.
- Stevenson F.J., 1994 - *Humus Chemistry*, 40.
- Teșu I., Baghinschi V., 1984 - *Energia și agricultura*, Editura Ceres, Bucuresti.
- Tipping E., 2002 - *Cation binding by humic substances*, 12:42.
- Zaccone C., Soler-Rovira P., Plaza C., Cocozza C., Miano T.M., 2009 - *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, 167:987.
- Zoja V. L. G., Barbora A., Miloslav P., Jiri K., 2009 - *Lignite pre-treatment and its effect on bio-stimulative properties of respective lignite humic acids*, Soil Biology & Biochemistry, 41:1894.
- Zhou P., Yan H., Gu B., 2005 - *Competitive complexation of metal ions with humic substances*, Chemosphere, 58:1327.