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OBTAINING OF HUMATE-BASED LIQUID FERTILIZERS TO BE USED IN THE RECULTIVATION OF SLAGHEAPS

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Abstract

During the experiments, the potassium humate used in obtaining the fertilizer was extracted from the coal mass, lignite, as a potassium carbonate solution. The humic/fulvic mix present in the fertilizer matrix contained approximately 70% organic acids, whereof 50% derive from humic acids and 20% from fulvic acids. The treatments made with the new humate-based liquid fertilizer AH-N applied in two doses
(150 l/ha) showed an increase of the mobile phosphorus in the soil as compared to the non-fertilized control, from 58.20 mg/kg to 70.61 mg/kg due to the fertilizer containing NPK in its matrix. As for the mobile potassium upon application of the liquid fertilizers, increases were noticed by the application of the AH-I liquid fertilizer in two doses (150 l/ha), 199.20 mg/ha as compared to the non-fertilized control 186 mg/ha. By the application of the new liquid fertilizer AH-U 150 l/ha, it increased the mobile potassium content in the soil to 188 mg/kg as compared to the non-fertilized control of 170 mg/kg at the end of the experiments.

Key words: *recultivation, slag heaps, humate-based liquid fertilizers.*

INTRODUCTION

Open-cast coal mining is an activity of an outstanding complexity and it has a direct action with negative effects of the environment. As is takes place on large areas and for a time-span of decades, its impact on the environment, in its turn, is very complex, with local and regional, short-term and especially long-term, cumulative effects, throughout the active mining period and after it (Pecingină et al., 2008). In the mining basins of Oltenia (Gorj, Vâlcea and Mehedinţi), 14,890 hectares were rendered economically useless, where of 12,208 hectares of agricultural land and 2,682 hectares of forested land, and until the end of the mining 26,472 hectares will be affected, where of 15,490 hectares of agricultural land and 10,982 hectares of forest (Dumitru şi colab., 2000). The materials deposited in the heaps are very heretogeneous from a physical and chemical points of view, they are lacking biological activity and are very diverse from a mineralogic point of view, which results in a low fertility potential (Baican et al., 2002). Fertilization and in certain cases amendment are important components of the recultivation procedures (Skousen and Zipper, 1996). Among the organic fertilizers, the best results on the slag heaps were provided by a sort of compost obtained from urban mud and fermented manure (Hall, 1992). Research for the production of organo-mineral fertilizers based on lignite started in our country two decades ago and currently have been approved such fertilizers which have a quality of humic amelioration of the soil with a low humus content, which have high characteristics of incorporation of the nitrogen and of other nutrients in an organo-mineral matrix, in forms which ensure the expansion of the term of the states assimilable in the soil, reduction of nitrogen loss by levigation, and reduction in intensity of the processes of free phosphate retrogradation (Dorneanu et al., 2008). These organo-mineral fertilizers on lignite support represent a factor of crop increase on soils poor in the main nutritive elements. The positive effect on various crops of the fertilizers containing humic substances has been widely studied (Arancon et al., 2006) (Unlu et al., 2011) (Akinci et al., 2009). A basic tendency in the structure and production of chemical fertilizers, outlined during the past 35 years, is the expansion and diversification of the range of liquid fertilizers, regardless of the technologies of use (Cioroianu et al., 2009). The first "research" on the possibility to use liquid fertilizers started about 170 years ago and coincides with the beginning of the synthesis of chemical substances based on nitrogen and ammonia (Cioroianu et al., 2009). The liquid fertilizers have special advantages due to their rapid and easy application, as well as to their higher agrochemical efficiency as compared to the classical solid fertilizers (Cioroianu et al., 2009).

MATERIALS AND METHODS

The experimental scheme comprised 9 variants in 4 repetitions: V1- Control (Non-fertilized); V2- AH-I - 100 l/ha; V3- AH-I - 150 l/ha; V4- AH-U - 100 l/ha; V5- AH-U - 150 l/ha; V6- AH-N - 100 l/ha; V7- AH-N - 150 l/ha; V8- KH - 100 l/ha; V9- KH - 150 l/ha.

For the experiment organized on the slag heap for the corm crop, a basic fertilization was performed before sowing, with solid NPK 15:15:15 - type fertilizers applied N – 90 kg/ha, P_2O_5 – 90 kg/ha, K_2O - 90 kg/ha, and the fertilizer physically applied per hectare was 600 kg. Before the sowing, a basic fertilization was performed with $N_{90}P_{90}K_{90}$ and after the sowing the humate-based liquid fertilizers AH-I, AH-U, AH-N and KH were applied in a concentration of 100-150 l fertilizer/ha in 450-500 l of water. The weeding operation was performed 60 days after sowing. Soil samples were taken 150 days after the implementation of the experiment, after the first treatment applied in three stages, the second treatment was applied in three stages, 210 days after the first treatment and soil samples were taken 60 days after the second treatment.

The procedure to obtain the liquid fertilizer consisted in the neutralization of the phosphoric acid concentration of 85% with potassium carbonate concentration of 98%, resulting in a solution that contained mono- and dipotassium phosphate. The reaction took place under a continuous stirring at a constant temperature of 250-300°C, gradually adding an amidic, nitrate and ammonium nitrogen source, and maintaining the reaction temperature, and as a result a complex mixture of macro-elements was obtained. Under continuous stirring conditions, at a temperature of 25-30°C, a solution of microelements (Fe, Cu, Zn, Mg, Mn, B) was chelated with EDTA disodium salt and mixed with a solution of potassium humate (Sîrbu et al., 2010). The scheme to obtain the NPK fertilizers is presented in Figure 1.

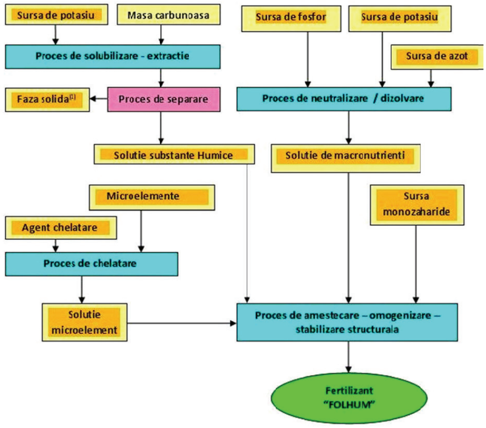

Figure 1. General scheme to obtain the NPK fertilizer with humic substances (according to Pârvan et al., 2012)

In the framework of the experiments performed, the potassium humate used to obtain the fertilizer was extracted from the coal mass, lignite, with the potassium carbonate solution.

The potassium humate extracted from lignite and used in obtaining the experimental fertilizer was thermally analyzed in the range of ambient temperature – 1000°C, in the air, with a 10 K/minute heating rate, simultaneously drawing the TGA (thermal gravimetric analysis), DTG (derivative *thermogravimetric analysis)*, DTA (differential thermal *analysis) and DSC (calorimetric analysis) curves* (Sîrbu et al., 2010). The measurements were made with a Perkin Elmer thermo balance which enabled mass determinations at an error of 1-2% in the temperature range of: ambient temperature – 1400°C and a heating rate of: 0.1-50 K/minute. The potassium humate obtained in the laboratory by alkaline extraction from lignite presented four main decomposition stages, namely: up to 85.3°C, loss 10.4%, which stage corresponded to drying by an endothermal process with a 57.9 J/g enthalpy; the second d process was also endothermal, in the range of 85.3-267°C, with an 11.6% mass loss and a 145.5 J/g process enthalpy. In the temperature range of 267-600°C the mass loss was 5.4%, when a slight exothermal effect could be noticed, with a 58.3 J/g enthalpy, the maximum heat eliminated being of 419.8°C for a heat flow of 1.12 mW. The fourth decomposition state took place in the temperature range of 600-800°C with a 4.7% mass loss. The humic/fulvic mix present in the fertilizer matrix contained about 70% organic acids, whereof 50% derive from humic acids and 20% from fulvic acids. The spectral analysis of the humic substances was made by Fourier transform infrared spectroscopy (*FTIR*) by means of the PerkinElmer Spectrum 100 and the VERTEX 70 spectrometers respectively, in the wave length range of 650-4000 cm^{-1} (Figure 2).

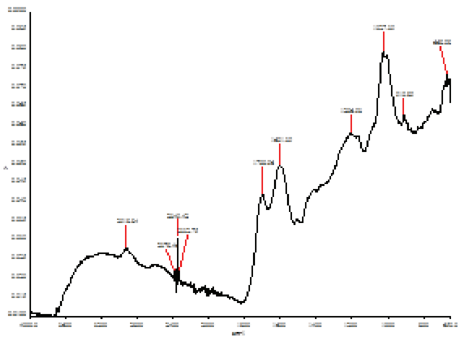

Figure 2. FTIR image of the humic acid extracted from the coal mass (lignite) (according to Pârvan et al., 2012)

Table 1. Composition of the AH-type fertilizers

Composition	AH FERTILIZERS		
	AH - I (g/l)	AH - U (g/l)	AH - N (g/l)
Humic acids	20.5	20.5	15.5
Total nitrogen (N)	90	55	165
Phosphorus (P_2O_5)	35	50	30
Potassium (K_2O)	35	50	30
Boron	0.2	0.15	0.18
Cobalt	0.005	0.005	-
Copper	0.1	0.15	0.2
Iron	0.25	0.3	0.4
Magnesium	0.1	0.15	0.4
Manganese	0.15	0.2	0.4
Molybdenum	0.005	0.005	-
SO_3	0.5	0.5	15
Zinc	0.1	0.15	0.2
EDTA	2.8	2.8	8.5
Total s.a	184.71	179.91	265.78

All the spectra were obtained by total infrared reflection with the ATR (Attenuated Total Reflectance) module. The resolution was 4 cm^{-1}, with the average of 4 up to 32 scans and the correction of the CO_2 and H_2O fund, in the transmittance mode.
Table 1 presents the physical - chemical characteristics determined for the fertilizers with humic acids obtained experimentally - AH-U, AH-N, AH-I, KH.

RESULTS AND DISCUSSIONS

Effects of the treatment with humate-based liquid fertilizers on the soil in the corn crop

In the first year of the experiment it was found that the application of one dose (100 l/ha) of the new fertilizer AH-I resulted in the reduction of the mobile potassium content in the soil as compared to the non-fertilized control. The values recorded were 144 mg/kg as compared to 170 mg/kg. Increase of the dose of humate-based liquid fertilizer to 150 l/ha resulted in the significant reduction of the K_{AL} in the soil, the value of the mobile potassium in the soil dropping to 120 mg/kg as compared to the value of the non-fertilized control, i.e. 170 mg/kg due to the fertilizer containing NPK in its matrix. By the application of the AH-U liquid fertilizer in two doses, the contents of mobile potassium in the soil increased significantly to 188 mg/kg as compared to the non-fertilized control of 170 mg/kg. Potassium humate applied in a 100 l/ha dose reduced significantly the K_{AL} content in the soil to 140 mg/kg as compared to the non-fertilized control of 170 mg/kg.

In the second year of the experiment on the slag heap the effects of the treatments with humate-based liquid fertilizers were noticeable by the drop of the mobile phosphorus in the soil as compared to the non-fertilized control. The potassium humate applied in one dose (100 l/ha) reduced the mobile phosphorus contents in the soil to the value of 46.72 mg/kg as compared to the non-fertilized control whose value was 47.95 mg/kg. As for mobile potassium, the application of the liquid fertilizers resulted in obvious increase following the application of the liquid fertilizer AH-I in two doses (150 l/ha): 199.20 mg/ha as compared to the non-fertilized control, 186 mg/kg, due to the fertilizer containing NPK in its matrix.

Table 2. Treatment efficiency in the two years of experimenting

No	Variant (average per repetitions)	First crop				Second crop			
		pH	ppm P_{AL}	ppm K_{AL}	% N	pH	ppm P_{AL}	ppm K_{AL}	% N
1	V1 (R1-R4)	7.78	58.20	170	0.15	7.68	47.95	186	0.18
2	V2 (R1-R4)	7.75	57.68	144	0.14	7.81	39.34	141	0.15
3	V3 (R1-R4)	7.80	43.67	120	0.14	7.74	41.83	199.2	0.18
4	V4 (R1-R4)	7.74	44.71	152	0.15	7.80	41.22	143.8	0.16
5	V5 (R1-R4)	7.72	47.42	142	0.13	7.80	39.96	152.6	0.14
6	V6 (R1-R4)	7.82	45.80	160	0.15	7.80	43.67	158.4	0.12
7	V7 (R1-R4)	7.52	70.61	188	0.15	7.82	31.35	116.2	0.12
8	V8 (R1-R4)	7.74	47.42	140	0.15	7.77	46.72	165.6	0.15
9	V9 (R1-R4)	7.77	49.04	168	0.15	7.75	42.45	187.4	0.18

The application of KH (potassium humate) in two doses (150 l/ha) also resulted in the increase of the mobile potassium contents in the soil as compared to the non-fertilized control, i.e. 187.40 mg/kg as compared to 186 mg/kg. By the application of one dose (100 l/ha) of AH-I, the total nitrogen in the soil dropped to 0.15% as compared to 0.18% in the non-fertilized control. The application of a double dose of AH-I (150 l/ha) did not change the total nitrogen contents in the soil. In the application of the treatment in the recultivation of the slag heap, one dose (100 l/ha) of AH-U reduced the total nitrogen contents in the soil to 0.16% as compared to 0.18% in the non-fertilized control. The increase of the AH-U liquid fertilizer dose resulted in the drop of the total nitrogen contents in the soil to 0.14% as compared to 0.18% in the non-fertilized control. The liquid fertilizer AH-N applied in one dose and two doses reduced the contents of total nitrogen in the soil to 0.12% as compared to 0.18% in the non-fertilized control. Potassium humate (KH) applied in one dose reduced the total nitrogen contents un the soil to 0.5% as compared to 0.18% in the non-fertilized control. By the application of a double dose of potassium humate the total nitrogen contents in the soil did not change.

CONCLUSIONS

By the application of treatments with humate-based liquid fertilizers in the recultivation of the Balta Unchiaşului slag heap we noticed as follows:

- the treatments performed with the liquid fertilizer AH-N in two doses (150 l/ha) resulted in the increase of the mobile phosphorus contents in the soil to 70.61 mg/kg as compared to the contents of 58.20 mg/kg in the first year of the experiment;
- in the case of the mobile potassium, the application of the liquid fertilizers resulted in increase, by application of AH-I in two doses (150 l/ha), to 199.20 mg/ha as compared to 186 mg/kg in the non-fertilized control. The application of the new liquid fertilizer AH-U 150 l/ha resulted in the increase of the mobile potassium in the soil to 188 mg/kg as compared to 170 mg/kg in the non-fertilized control, in the second year of the experiment;
- the use of the new liquid fertilizers AH-I, AH-N and AH-U in the two years of experiments on the corn crop of the slag heap had positive effects on the soil by the increase of its nutrient contents.

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