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Production and Assessment of Biological Activity of Granular Complex Humic Fertilizers

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Abstract

The paper presents the results of biological tests of granular complex humic fertilizers (CHF) with the addition of carbamide (urea) and simple superphosphate. CHF samples were obtained from lignite (brown coal) of the Tisul deposit (Kaychak plot, Kemerovo Region), their production method is given. Samples of complex granular fertilizers, initial coal and humic acids (HA) were characterized using ^{13}C CP/MAS NMR, technical and elemental analysis. An integral indice, *i.e.* the index of phytoactivity (IP) that was calculated as the average value of the sum of indicators of the germinative energy, the seedling height (SH) and root length of seeds was used for objective testing. It was performed on seeds of spring wheat Iren by soaking them in an aqueous solution of CHF. Seeds were germinated under the conditions of State Standard GOST 12038–84. The effect of major components that were HA and mineral additives contained in the composition of CHF was determined. It was found that alongside with the composition of CHF, the functional group composition parameters might affect biological activity. It was demonstrated that the synergistic effect of HA and introduced mineral additives was observed. The presence of HA in CHF allowed decreasing the concentration of the solution to soak seeds without decreasing its biological activity. The tested CHF showed high phytoactivity (IP = 1.19–1.45). The maximum biological activity was noted in samples treated with superphosphate. The ability of HA to decrease the suppressive effect of large concentrations in solutions of mineral fertilizers was determined.

Kew words: humic substances, biological activity, granular complex humic fertilizers

INTRODUCTION

Humic substances (HS) make up a major part of brown coal organic mass that are currently not of great interest as a source of energy. In this regard, the issue of complex refining of brown coal is important. Lately, an interest towards HS used as efficient plant growth stimulators has significantly increased [1–3]. Since the content of HS in brown coal may reach 90 %, these raw materials are a promising source for their preparation [4].

Earlier, HS and humic acids (HA) were used as salts, *i.e.* sodium, potassium, and ammonium humates. They act now as one of the components of complex fertilizers. These fertilizers show a significant increase in biological activity due to more rational formulations including both stimulators (HA) and macro-/microelements of plant nutrition [5]. Their use allows significantly lowering distribution rates of mineral fertilizers due to the ability to increase the efficiency of using nutrients by plants both from soil and introduced fertilizers.

TABLE 1

Results of technical and elemental analysis of brown coal, humic acid (HA), and granular humic fertilizers (CHF), %

Samples	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	$(O + N + S)^{daf}$, by difference	$(HA)_t^{daf}$, (HumNa)	$(HA)_t^{daf}$, (HumK)	Introduced with mineral fertilizers	
									N^d	$P_2O_5^d$
Brown coal	8.30	10.32	48.26	61.44	5.04	33.52	22.14	24.98	–	–
HA from HumNa	3.76	1.92	n/d	59.79	3.47	36.74	–	–	–	–
CHF-1	n/d	n/d	n/d	50.59	4.15	45.26	5.57	–	–	–
CHF-2	n/d	n/d	n/d	34.10	5.53	60.37	7.37	–	25.19	–
CHF-3	n/d	n/d	n/d	36.28	3.27	60.45	5.09	–	5.65	5.37

Notes. 1. daf is dry ash-free condition of the sample; W^a is moisture of analysis sample; A^d is ash content for a dry sample; V^{daf} is volatile matter content; C^{daf} is carbon content; H^{daf} is hydrogen content; O^{daf} is oxygen content; N^{daf} is nitrogen content; S^{daf} is total sulphur content; $(HA)_t^{daf}$ is yield of free humic acids; HumNa is sodium humate; HumK is potassium humate; d indicates for the dry condition of the sample. 2. N/d – not determined.

This paper presents the results of determination of biological activity for several CHF samples in wheat seeds Iren.

EXPERIMENTAL

CHF samples were obtained from raw coal of the Tisul' deposit (Kaychak plot) having the following characteristics (Table 1). Humic acids isolated from sodium humates (HA HumNa) obtained by the method of determining the yield of free HA [6] (1 % NaOH solution, 98 °C, 2 h).

CHF-2 and CHF-3 samples were obtained by mixing appropriate humic fertilizers with carbamide and superphosphate (Table 2).

Thetechnique of generation of CHF granules was described in [7] and consisted of the following: 1) brown coal was pulverized using a hammer mill to a particle size of 0–3 mm; 2) crushed coal was mixed with an aqueous solution of alkali for 30 min using a paddle mixer; 3) mineral fertilizers were added into a mixer and stirring was continued for 10 min; 4) the resulting paste was granulated using extruder; 5) the granules were dried in the infrared dual zone dryer. Characteristics of CHF samples without additives and with the addition of urea and superphosphate are given in Table 3. Humic acids are part of the granules as HumNa.

The group composition of initial coal samples, HA isolated from it and the proposed complex fertilizers was defined by ^{13}C NMR CP/MAS techniques. The data are presented in Table 4.

High resolution ^{13}C solid state NMR spectra were removed using a Bruker Avance III 300 WB spectrometer at a frequency of 75 MHz and sample rotation frequency of 5 kHz. The cross-polarizing technique with rotation under magic angle was used.

Structural group parameters of all samples can be calculated by ^{13}C NMR CP/MAS spectroscopic results [2, 7–10]:

a) aromaticity degree

f_a = CAr–OH + CAr;

b) hydrophilic/hydrophobic characteristic

$f_{h/h}$ = (C=O + COOH(R) + Car–OH + CO–Alk–O + Calk–O) / (CAr + CAlk);

TABLE 2

Characteristics of the used mineral fertilizers

Fertilizers	Chemical formula	Mass fraction of acting ingredient, %		Moisture content, %, no more than
		N	P_2O_5	
Carbamide (urea)	$(NH_2)_2CO$	46	–	0.5
Simple superphosphate	$Ca(H_2PO_4)_2 \cdot 2CaSO_4$	20	19	3.5

TABLE 3

Characteristic of the generated CHF samples

Samples	Moisture content, %	Coal residue yield, %*	Yield of water-soluble HA, %*	Introduced with mineral fertilizers, %*	
				N	P_2O_5
CHF-1	35.26	94.43	5.57	–	–
CHF-2	25.96	67.44	7.37	25.19	–
CHF-3	27.75	83.89	5.09	5.65	5.37

*For the dry state of the sample.

c) aromaticity/alifaticity

$f_{ar/al}$ = (Car–OH + CAr)/(CO–Alk–O + Calk–O + CAlk)

The results demonstrated that all samples were highly aromatic. Additionally, samples of CHF-1, CHF-2, and CHF-3 contained more carbonyl (220–167 ppm) and carboxyl (187–165 ppm) groups containing oxygen at an alkyl carbon (90–48 ppm) in comparison with initial coal and HA from it.

Analysis of ^{13}C NMR data demonstrated that, alongside with the composition of CHF, the composition of functional groups could affect their biological activity. An increase in phytoactivity jointly with a rise in indicators of structural characteristics is traced: aromaticity degree (f_a), hydrophilic/hydrophobic characteristic ($f_{h/h}$) and a parameter reflecting the ratio of aromatic and aliphatic fragments in CHF organic mass ($f_{ar/al}$, mass aromaticity/aliphaticity).

Following GOST [11], biological activity of CHF was defined by GOST 12038–84 methods [12], as well as from [13] – by the value of index of phytoactivity (IP) taking into account the germinative energy (GE) of seeds, root length (RL) and seedling height (SH). Index of phytoactivity is a composite index and it is calculated as average value of the sum of GE, RL and SH indicators expressed in unit fractions:

IP = (GE + RL + RL)/(3 · 100)

where GE, RL and RL are average values for three trays (the percentage in relation to the reference sample).

In each experiment, a part of seeds was treated with 0.0005 and 0.005 % HA solutions, and a part was treated with distilled water (reference sample). Selection of concentrations was based on the fact that HA in concentrated solutions exerted the suppressive action on plants [14]. Thus, it was found by practical consideration that the concentration of an HA solution over 0.005 % had the suppressive effect, and a concentration of less than 0.0005 % turned out to be ineffective.

Experiments on defining the contribution of carbamide and superphosphate contained in CHF into their biological activity were additionally performed. For the experiments, 0.00158

TABLE 4

Integral values for spectral regions of ^{13}C CP/MAS NMR spectra of samples of brown coal, humic acids (HA), and complex granular fertilizers (CHF)

Samples	Chemical shift, ppm							Structural parameters			IP*
	220–187	187–165	165–145	145–108	108–90	90–48	48–5				
	C=O	COOH	C_{ar}–OH	C_{ar}	$C_{O\text{-}alk\text{-}O}$	C_{alk}–O	C_{alk}	f_a	$f_{h/h}$	$f_{ar/al}$	
Brown coal	1.23	2.91	12.72	53.10	0	9.19	20.84	65.8	0.35	2.19	–
HA from HumNa	1.16	4.16	13.78	51.76	0	8.88	20.26	65.5	0.39	2.25	–
CHF-1	1.90	5.57	8.47	50.71	0	11.26	22.06	59.2	0.37	1.78	1.19
CHF-2	1.66	5.35	12.24	49.20	0	11.24	20.31	61.4	0.44	1.95	1.32
CHF-3	1.69	5.47	11.74	49.36	0	10.82	20.93	61.1	0.42	1.92	1.45

*Index phytoactivity (IP) with a concentration of CHF solutions of 0.0005 %.

and 0.0158 % solutions of carbamide, as well as 0.00034 and 0.0034 % solutions of superphosphate were prepared. Concentrations of solutions of mineral fertilizers corresponded to those in the tested CHF.

Seeds were germinated in special germinators between layers of moist filter paper. The repeatability of the experiment was triple: by 50 seeds in a tray for each concentration of fertilizers and the same for control; GE, SH and RL were measured on the fifth day. Seeds were germinated at a constant temperature of 20 °C in the dark.

It is noteworthy that all the measured indicators of seeds had the tolerance spread. Thus, the coefficient of variation of SH and RL was no more than 27.58 %, and in control trays – 32.54 % when measuring seeds of treated CHF, which testifies the uniformity of measurements. This coefficient represents the ratio of the standard deviation to the mean expressed as a percentage. A sequence of data is considered to be uniform, if the coefficient of variation does not exceed 33 % [15].

RESULTS AND DISCUSSION

The results of determination of biological activity in proposed CHF are given in Table 5. Outcomes for all control trays were averaged for more visible determination of biological activity of all fertilizers, as well as for an opportunity to compare their efficiency.

The use of humic fertilizers CHF-1 as 0.0005 % solution turned out to be efficient: the index of phytoactivity was 1.19. It was also noted that seeds treated with CHF-1 solutions had more developed root system. Roots in a reference sample were less developed.

Tests of HF-2 sample containing 25.19 % of nitrogen (as carbamide) alongside with HA demonstrated positive results. Thus, 0.0005 % solution of the fertilizer demonstrated IP of 1.32, and 0.005 % solution – 1.19.

A sample of CHF-3 demonstrated the best result. We managed to increase IP to 1.45 and 1.44 at concentrations of the solution of 0.0005 and 0.005 % due to the addition of 5.65 % of nitrogen and 5.37 % of phosphorus (as superphosphate).

Based on the data obtained, one could conclude that the use of CHF of a certain composition has positive effects on germination of wheat seeds (Figs. 1–4).

At solution concentration of 0.0005 % of CHF-1 sample, IP was 1.19, in other words, the mean increment of GE, SH and RL was 19 %. A concentration of 0.005 % of the same sample proved to be ineffective (IP = 1.09). The use of 0.00158 % solution of carbamide gave an increase in indicators at a level of 5 % (IP = 1.05), low GE was the reason for this. At a concentration of 0.0158 %, carbamide had suppressive effect.

TABLE 5

Effect of mineral additives for efficiency of fertilizers

Samples	RL, cm	SH, cm	GE, %	IP	Structural parameters		
					f_a	$f_{h/h}$	$f_{ar/al}$
Reference sample*	8.2	7.9	100	1.0	–	–	–
Solution of 0.0005 % of CHF-1	10.2 (+24.9)	10.1 (+27.4)	104.1	1.19	59.2	0.37	1.78
The same, 0.005 %	8.8 (+7.9)	8.3 (+5.32)	113.2	1.09			
Solution of 0.0005 % of CHF-2	11.2 (+37.4)	12.2 (+54.8)	104.0	1.32	61.4	0.44	1.95
The same, 0.005 %	10.3 (+26.6)	9.9 (+25.2)	106.7	1.19			
Solution of 0.0005 % of CHF-3	12.8 (+56.8)	12.8 (+62.5)	116.5	1.45	61.1	0.42	1.92
The same, 0.005 %	12.8 (+57.5)	12.6 (+60.1)	113.9	1.44			
Carbamide solution 0.00158 %	9.8 (+19.7)	8.9 (+13.9)	82.3	1.05	–	–	–
The same, 0.0158 %	2.2 (−73)	2.1 (−74.2)	91.2	0.48	–	–	–
Superphosphate solution 0.00034 %	8.9 (+9.6)	7.9 (+0.7)	100.0	1.03	–	–	–
The same, 0.0034 %	9.8 (+21.4)	9.9 (+26.3)	111.4	1.19	–	–	–

Notes. 1. RL is root length, SH is seeding height, GE is germinative energy of seeds, and IP is index of phytoactivity. 2. An increase in the indicator compared to the averaged reference sample is indicated in brackets, %.

*Average by all experiments.

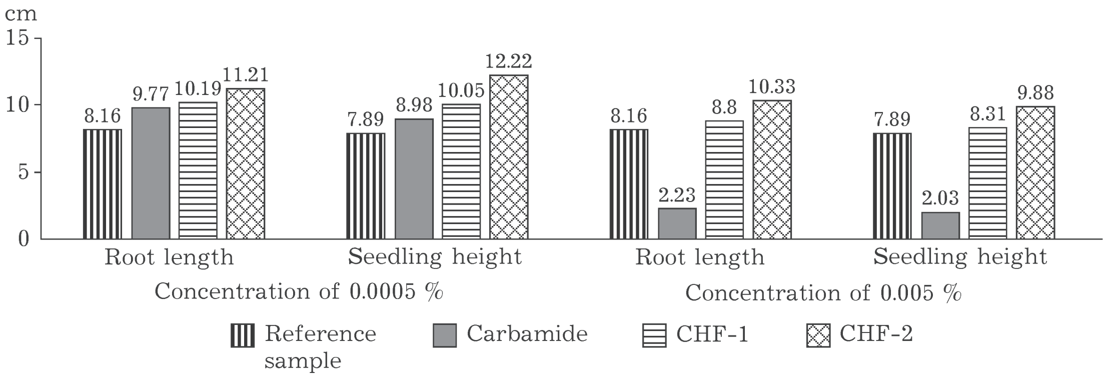

Fig. 1. Seedling height (SH) and root length (RL) when testing samples of CHF-1, CHF-2, and carbamide.

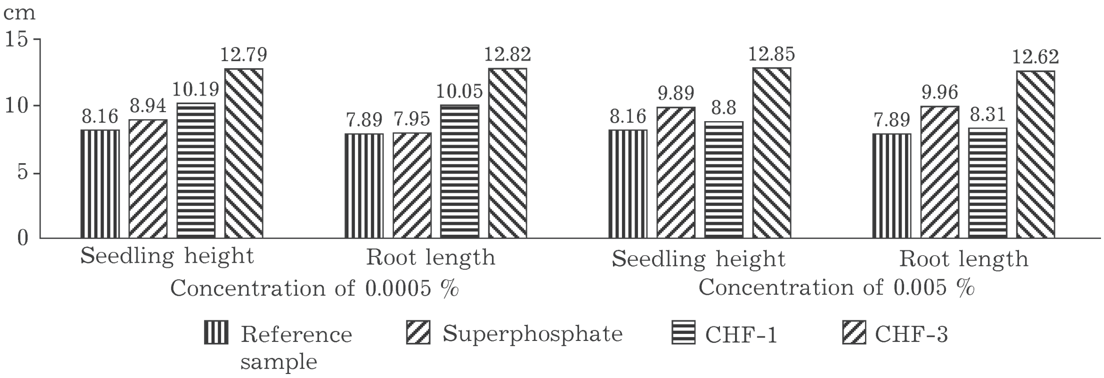

Fig. 2. Seedling height (SH) and root length (RL) when testing samples of CHF-1, CHF-3, and superphosphate.

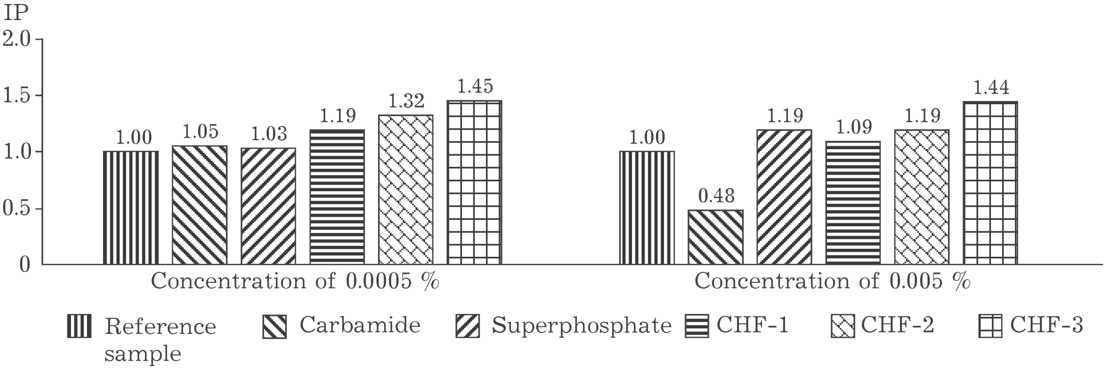

Fig. 3. Index of phytoactivity (IP) of tested samples of CHF and mineral fertilizers.

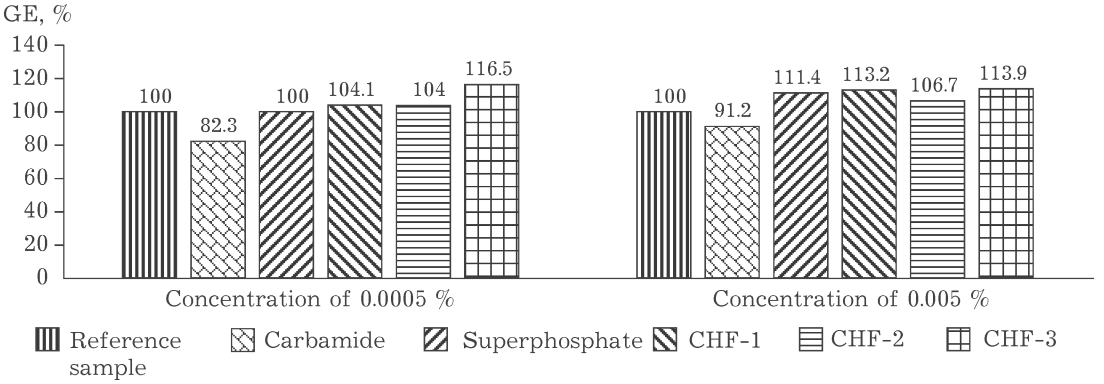

Fig. 4. Germinative energy (GE) of seeds of samples of CHF and mineral fertilizers.

The application of 0.00034 % solution of superphosphate did not show strongly marked effects, however, in its turn, the use of 0.0034 % concentration resulted in an increase of indicators by 19 % (IP = 1.19).

As for complex fertilizers, CHF-2 sample demonstrated 32 and 19 % of an increase, respectively. Low biological activity of fertilizers in the concentrated solution is related to the depressing effects of an excess of carbamide, but the presence of HA softened this depressing action.

In its turn, CHF-3 sample demonstrated the best result out of all fertilizers due to the synergistic effect of HA and superphosphate (IP = 1.45).

It was found that the differences between the results of fertilizer and control testing were statistically significant. Thus, Student's t-test during comparison of the results of CHF-3 and control testing was 6.23, and the confidence level was less than 0.001, which speaks of the presence of highly reliable statistically significant difference. The confidence level for all other fertilizers also does not exceed 0.05.

Experimental results indicate that the addition of a small amount of HA into mineral fertilizers allows decreasing their required amounts without weakening biological activity, which is confirmed by CHF-3 sample (see Table 4).

CONCLUSION

By the result of determining biological activity of proposed complex granular humic fertilizers (CHF) and components included in them, one could conclude that the synergistic effect of humic acids (HA) and mineral additives is observed, and their joint use allows decreasing the initial distribution rates of mineral additives. The resulting CHF showed high levels of phytoactivity (IP = 1.19–1.45). It was found that HA could decrease the suppressive action of large doses of mineral fertilizers for wheat sprouts.

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