Chemistry of Natural Compounds, Vol. 44, No. 1, 2008

PRODUCTION OF HYDROXYHUMIC PREPARATIONS FROM TURF

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One of the promising methods for activating turf for chemical modification is cavitation treatment in aqueous base in cavitation devices [1]. Turf subjected to cavitation treatment in various media changes its chemical composition and is activated. Cavitation treatment consists of explosive boiling of an aqueous suspension of turf upon collision with a barrier, partial destruction of turf occurs due to grinding of the solid phase by a rotor rotating at high speed that is fixed to the stator of the cavitation device. The rotorary cavitation device (disperser) is constructed with a rotor rotation frequency of 3000 rpm according to a patent [1]. However, oxidation of turf in various media by cavitation treatment has not been systematically studied in the literature. Therefore, the goal of our work was to investigate oxidation of turf by H_2O_2 in aqueous base during cavitation treatment in order to develop an effective method for producing sodium hydroxyhumates [1].

The starting turf had the following composition (calc. for abs. dry substance), %: bitumen, 3.7; total N, 2.1; organic substances, 72.1; of these, humic acids, 24.6; fulvic acids, 23.4. Table 1 presents results from a study of the effect of the time of cavitation treatment on the yield of water-soluble organic substances (WSOS) from turf.

Increasing the time of cavitation treatment of turf at 60°C in the presence of H_2O_2 in aqueous base increases the concentration of WSOS in the resulting extracts from 22 to 39 g/L.

Table 2 gives data for the effect of NaOH concentration on the N content in the solid residue and the C content in humic and fulvic acids in the resulting liquid humic fertilizers.

Increasing the NaOH concentration decreases the N content in the dry residue from 1.9 to 0.9% and increases the total amount of WSOS and C of humic and fulvic acids in the liquid phase of the resulting fertilizers (Table 2). The highest yield of fulvic acids is observed for 10 mass % base concentration. This is probably due to more extensive oxidation of humic substances of the turf.

Thus, the proposed method can produce the highest yield of WSOS in the desired product (liquid phase) by a simpler and less energy-intensive method compared to analogous ones [2, 3].

The chemical composition of the destruction products from the liquid phase after turf oxidation was studied (sample 7, Table 2) by isolating hydroxyhumic acids (HHA) by acidification with H_2SO_4 (0.5 N).

The HHA composition was (found, %): C 62.5, H 5.7, N 1.3, O 30.5, OH_{phen} 1.9, COOH 4.3. The HA composition (found, %): C 56.2, H 6.3, N 2.5, O 35.0, OH_{phen} 3.1, COOH 2.2. Thus, hydroxyhumic acids contain more C and less H and N than HA of the starting turf.

Cavitation treatment in aqueous base causes partial base hydrolysis of humic substances. This is due to cleavage of easily hydrolyzed forms of N and its decreased content in the humic acids. The hydroxyhumic acids contain more COOH groups and less phenolic OH groups than the starting humic acids.

Thus, cavitation of turf with H_2O_2 in aqueous base oxidizes humic substances, probably due to phenolic structures, the hydroxyl groups of which are oxidized to COOH groups.

The growth-stimulating activity of hydroxyhumates from turf was studied by determining the germination of 100 spring wheat seeds of variety Altai vista by moistening them in Petri dishes in 0.01 and 0.03% solutions containing sample 7 hydroxyhumate (see Table 2). The controls were seeds grown in distilled water (Table 3 gives the data). It can be seen that adding sodium hydroxyhumate at concentrations of 0.01 and 0.03% increases the germination of spring wheat compared with the control by an average of 10-12.5%.

Thus, turf oxidation products obtained by cavitation treatment with H_2O_2 in aqueous base solution are effective plant growth stimulators.

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Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 109-110, January-February, 2008. Original article submitted October 16, 2006.

0009-3130/08/4401-0142

TABLE 1. Effect of Cavitation Time on WSOS Yield for Turf Oxidation by H_2O_2 in NaOH (2%)*

Sample	Oxidation time by cavitation, min	C content, g/L		
		total	humic acids	fulvic acids
starting turf	-	80.5	41.2	39.3
1	15	22.3	12.2	10.1
2	30	26.4	15.2	11.2
3	45	32.5	19.3	13.2
4	60	39.3	22.2	17.1

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* - Time of preliminary basic cavitation treatment, 15 min; amount of H_2O_2, 5% of absolute dry mass of turf.

TABLE 2. Effect of NaOH Concentration on N Content in Solid Residue and Contents of Humic and Fulvic Acids in Liquid Phase for H_2O_2 Oxidation of Turf*

Sample	Base concentration, %	N content in solid residue, %	C content, g/L		
			total	humic acids	fulvic acids
Starting turf	-	2.1	80.5	41.2	39.3
2	2	1.9	26.4	15.2	11.2
5	4	1.8	39.2	23.1	16.1
6	6	1.7	75.3	56.2	19.1
7	8	1.0	97.4	86.2	11.2
8	10	0.9	105.2	41.1	64.1
9	2**	1.8	28.5	16.3	12.2

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* - Time of preliminary basic cavitation treatment,15 min; amount of H_2O_2, 5% of absolute dry mass of turf; time of oxidation by cavitation treatment, 30 min.

** - KOH used as the base.

TABLE 3. Test Results for the Effect of Produced Sodium Hydroxyhumate on Germination of Spring Wheat Seeds*

Version	Germination, %			
	expt. 1	expt. 2	expt. 3	average
Control (without stimulator)	87	89	88	88
Hydroxyhumate 0.01%	96	97	98	97
Hydroxyhumate 0.03%	99	99	99	99

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* - Sample 7 of sodium hydroxyhumate.

Production of Hydroxyhumates from Turf. The starting material was peat turf of Odintsov deposit in Altai Krai with about 25% decomposition and 22.1% ash content that was produced at OOO NPO Tellura-Bis (Biisk). The chemical composition of the starting turf was determined. The moisture and ash contents of the turf were established by drying and ashing in a muffle furnace according to GOST 11305-83 and 11306-83.

The moisture content of the starting turf was 49.3%. The total N content was determined by the Kjeldahl method [4]; total C content (organic substances), by the photocolorimetric Turin potassium bichromate oxidation method in H_2SO_4 [4]; C content of humic substances, by the photocolorimetric Turin method after extraction of humic substances from turf by a basic solution of sodium pyrophosphate according to GOST 9517-94; the content of humic acids, after their precipitation by H_2SO_4

(0.5 N) with subsequent dissolution in base and Turin photocolorimetric titration [4]; the content of fulvic acids, by the difference between the total content of humic substances and the content of humic acids.

Hydroxyhumates from turf were produced as follows. A weighed portion of starting turf (2.0 kg) was treated by cavitation for 15 min in aqueous NaOH (2.0-10%) in a 1:2 ratio in a 10-L cylindrical thermostatted reactor combined with a rotary cavitation device with rotor rotation frequency 3000 rpm. Then it was treated with H_2O_2 (0.05 kg H_2O_2 per kg absolute dry turf) at 60°C for 15-60 min.

Then the resulting suspension was poured for settling into a 10-L polyethylene bottle. Samples (1 L) were taken to analyze the resulting liquid humic fertilizers. The solid was centrifuged. The liquid phase was separated (desired product). The contents of total organic carbon and carbon of humic and fulvic acids were determined by a modified Turin method [4]; in the solid residue, the N content by the Kjeldahl method [4].

Hydroxyhumic preparations were isolated by centrifuging the liquid phase (0.05 L) acidified at 25°C by aqueous H_2SO_4 (0.5 N) to pH 1. The precipitate of hydroxyhumic substances (HHA) was centrifuged and washed three times with distilled water to remove H_2SO_4 ($BaCl_2$ control).

Humic acids were isolated analogously from starting turf (ST). The ash content was 5 and 7% (HHA and HA, respectively). The N content was determined by the Kjeldahl method, the C and H contents, by ignition in a stream of oxygen. The O content was calculated by difference; the contents of total acidic and carboxylic groups, by chemosorption by $BaCl_2$ and calcium acetate methods [4].

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