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Oxidation of Brown Coals With Hydrogen Peroxide in the Presence of Oxalic Acid for the Subsequent Production of Humic Soil Improver For Degraded Soils

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Abstract:

The article describes the results of oxidizing Angren brown coal with hydrogen peroxide in the presence of oxalic acid and producing a humic soil improver—calcium humate—from the oxidation products, enhancing soil structure by adding quicklime to the oxidized brown coal. The possibility of obtaining a moisture-absorbing humic improver by treating brown coal with oxalic acid, followed by oxidation with hydrogen peroxide and polymerization of humic acids using quicklime, is demonstrated.

Keywords: improver, brown coal, humic acids, oxidation, calcium, lime, oxalic acid.

Introduction. Analysis of numerous studies shows that soil degradation processes are intensifying worldwide. Chemical soil degradation, caused by agricultural production, is widespread. Soil contamination occurs due to global processes and excessive use of fertilizers, wastewater irrigation, and unconventional fertilizers, leading to reduced agronomic properties. Soil is a "naturally historical body" formed from the interaction of climate, rocks, relief, and vegetation, possessing fertility. It differs from other natural bodies by a range of unique properties, primarily the presence of humus. Soil consists of solid, liquid, gaseous, and living phases and is considered an independent natural system. Soil degradation manifests in various forms due to anthropogenic factors, with different factors causing different degradation types. Several forms often coexist, with varying degrees of development. It is crucial to note that all organomineral fertilizers can be classified as soil improvers. The term "amelioration" refers to enhancing soil fertility through drainage or irrigation, specifically in chemical amelioration. Humic fertilizers are effective chemical improvers due to their adsorption and ion-exchange properties and aid in reclaiming saline soils.

In the work [5], a method for obtaining soil improvers is presented, which involves the hydrolysis of natural humic-containing compounds in an aqueous ammonia solution. To enhance the structuring action of the improver, urea is additionally introduced into the ammonia solution at a ratio of 20-100% based on anhydrous ammonia. The hydrolysis of humic-containing compounds with ammonia is carried out to a pH of 8.5-10.5. The improver exhibits high structuring activity, particularly in clay and loamy soils.

In the work [6], a stabilizer based on a carbonate reagent is used for soil deacidification with the following component ratios: 55-57% chalk, 0.55-0.75% carbonate reagent, and the remainder being water. A composition for soil improvement made from washed and granulated (approximately 1 mm in diameter) coal waste is proposed. Organic additives, bone meal, K_2SO_4, and $(NH_4)_2SO_4$ can be introduced into it, with the coal waste comprising 60-80% of the composition [7]. The use of organic material to improve soil—specifically its structure, air and water permeability, moisture absorption, and retention capacity for moisture and nutrients—has been proposed. This involves the reaction of a basic inorganic material containing magnesium or calcium oxide with a mineral acid applied to the surface of the organic material, such as lignite or peat. Mineral acids used include H_2SO_4, H_3PO_4, or HNO_3, and inorganic materials include magnesium hydroxide, basic magnesium fertilizers, and dolomite. The product of the acid and basic inorganic material reaction constitutes more than 5% of the mass of the organic carrier [8].

A composition for soil treatment and a method for its use have been proposed, which includes an alkaline earth element intended for neutralizing acidic soils, particularly in the subsoil layer where most plant roots are located. The alkaline earth element is used in the form of a water-soluble complex with an organic acid derived from coal. The organic acid is present in the composition at a concentration of 0.04-85%, providing a pH of 4-10. The organic acid solution is prepared by treating coal with hot (200°C) water in a reactor with a stirrer, where steam is supplied at a pressure of 8.0 MPa. The solution, separated from the coal, has a total acidity predominantly determined by carboxyl groups (90%) and phenolic groups (the remainder). The composition transports calcium into the subsoil layer (up to 45 cm) by 90-95% (with $CaCO_3$ constituting 20%) and significantly raises its pH [9].

One of the main requirements for a soil improver is maximum cation exchange capacity, determined by the number of functional groups capable of ion exchange (–COOH and –OH), which are present in low quantities in lignites. The number of acidic groups capable of ion exchange can be increased through oxidation. By using oxidized brown coal from the Gusinoozerskoye deposit on saline sodic soils, a significant increase in yield was achieved due to its desalting effect [10].

Chemical amelioration of soils with organomineral fertilizers based on oxidized brown coals is not limited to desalting saline lands. It is also effective for decontaminating water and soil environments from radioactive elements, heavy metals, and unused herbicides left in the soil. This is all thanks to humic acids, which act as natural detoxifiers in this context [11-15].

Additionally, it is important to note that soil structure significantly influences agronomic properties and soil fertility. Structured soils create more favorable conditions for water, air, heat, and nutrient regimes. Calcium humate is a highly effective soil structuring agent, with a molecular weight ranging from 1,000 to 100,000 depending on the molecular weight and number of hydrocarbon radicals. The application of calcium humate increases capillary and field moisture capacity and soil permeability, improves the structure and water retention of soil aggregates, and enhances moisture retention capacity and air exchange in the root zone of the soil.

Based on the above, this work investigates the processes for obtaining a humic ameliorant—calcium humate. To increase the yield of humic acids and enhance the number of functional groups, brown coal from the Angren deposit was oxidized with hydrogen peroxide in the presence of oxalic acid.

In the experiments, a representative sample of coal powder of grade BPK was used, which, after drying to an air-dry state and grinding in a ball mill to a particle size of 0.25 mm, had the following composition (weight %): moisture 5.11; ash 11.7; organic matter 83.68; humic acids 13.18% based on organic mass. The oxidation process was conducted with hydrogen peroxide concentrations of 10-30%, oxalic acid at 60%, and a weight ratio of coal (organic part) : H_2O_2 : $H_2C_2O_4$ of 1 : (0.1-0.5) : 0.01.

The experiments were carried out as follows: first, the coal was treated with oxalic acid in a mechanical mortar at a coal : $H_2C_2O_4$ ratio of 1 : 0.01 for 30 minutes. The treated coal remained in a free-flowing state. The resulting mass was then transferred to a reactor, where a hydrogen peroxide solution was added while stirring. Their interaction occurred over a period of 2 hours. During the oxidation of brown coal with hydrogen peroxide, the temperature of the reaction mass rose to 50-80°C. In all experiments, at the end of the oxidation process, the reaction mass was dried to an air-dry state, and the ash content, moisture, organic matter, and yield of humic and fulvic acids were determined. The ash content was determined according to GOST 11022-75, moisture according to GOST 11014-70, organic matter as the difference between 100 and the sum of the percentage contents of ash and moisture, and the yield of humic acids according to GOST 9517-76.

Alkali-soluble organic substances were extracted from oxidized coal using a 2% aqueous solution of sodium hydroxide in a tenfold ratio to the weight of the coal, with an extraction time of 2 hours at boiling temperature. A triple extraction method was employed, and the completeness of extraction was monitored by the color of the extractant, which turned colorless upon complete extraction of humic acids. The solid phase was separated from the liquid by centrifugation, and the total volume of the solution was measured. An aliquot was taken, dried to a constant weight, weighed, and then ashed. The difference between the dried precipitate and the ash content provided the amount of alkali-soluble organic substances [16].

The solid phase of the oxidized coal, after the removal of alkali-soluble organic substances, represented residual coal. It was thoroughly washed with distilled water, dried to a constant weight, and the yield based on organic mass was determined. The difference between the amounts of alkali-soluble organic substances and humic acids provided the content of fulvic acids in the oxidized coal. The results of the experiments are presented in Table 1, which shows how the composition of the oxidized coal changes based on the norm and concentration of oxidizing reagents. The highest amount of humic acids, 64.17%, was found in the oxidized coal produced using 10% hydrogen peroxide, 60% oxalic acid, and a mass ratio of coal : H_2O_2 : $H_2C_2O_4$ = 1 : 0.3 : 0.01. A similar amount of humic acids, 63.7%, was also found in coal oxidized with 10% hydrogen peroxide and 60% $H_2C_2O_4$ at a mass ratio of coal : H_2O_2 : $H_2C_2O_4$ = 1 : 0.5 : 0.01. This indicates that the oxidation of brown coal from the Angren deposit with hydrogen peroxide in the presence of $H_2C_2O_4$ increases the content of humic acids from 13.18% to 64%.**

The content of functional groups in the initial, oxidized, residual coals, and in the humic acids of both the initial and oxidized coals was determined. The oxidized coal was obtained using 10% H_2O_2, 60% $H_2C_2O_4$, and a mass ratio of coal : H_2O_2 : $H_2C_2O_4$ = 1 : 0.1 : 0.01. Functional groups were identified using a sorption method based on the ability of active acidic groups in the organic mass to react with barium hydroxide and calcium acetate in an aqueous medium [17-26]. The results are presented in Table 2.

As seen from the table, the oxidation of coal with hydrogen peroxide in the presence of $H_2C_2O_4$ increases the content of active functional groups, both in the oxidized coal itself and in its humic acids. The initial coal contained 0.75 mg-eq/g of carboxyl groups and 1.578 mg-eq/g of phenolic hydroxyls; in the oxidized coal, these figures rose to 3.87 mg-eq/g and 2.7 mg-eq/g, respectively, while in the humic acids of the oxidized coal, they reached 6.77 mg-eq/g and 3.98 mg-eq/g. This study demonstrated that the oxidation of brown coal from the Angren deposit with hydrogen peroxide in the presence of $H_2C_2O_4$ significantly enhances its content of humic acids and active functional groups.

Table 1. Yield of Coal Oxidation Products Depending on the Norm and Concentration of Hydrogen Peroxide and Oxalic Acid

Ratio Coal: H_2O_2 : $H_2C_2O_4$	Yield of oxidation products, %	Determined components in % of the organic part of oxidized coal			
		Alkali-soluble substances	Humic acids	Fulvic acids	Residual coal
Concentration of hydrogen peroxide 10%, oxalic acid 60%					
1 : 0.1 : 0.01	108.57	53.38	50.2	3.18	46.62
1 : 0.2 : 0.01	109.41	63.07	59.31	3.76	36.93
1 : 0.3 : 0.01	110.28	68.35	64.17	4.38	31.65
1 : 0.4 : 0.01	111.24	66.36	61.18	5.18	33.64
1 : 0.5 : 0.01	111.82	69.49	63.7	5.79	30.51
Concentration of hydrogen peroxide 20%, oxalic acid 60%					
1 : 0.1 : 0.01	105.49	45.79	41.34	4.45	54.21
1 : 0.2 : 0.01	105.97	52.42	47.22	5.2	47.58
1 : 0.3 : 0.01	106.26	54.72	50.36	4.36	45.28
1 : 0.4 : 0.01	107.94	53.96	50.85	3.11	46.04
1 : 0.5 : 0.01	108.22	60.46	54.51	5.96	39.54
Concentration of hydrogen peroxide 30%, oxalic acid 60%					
1 : 0.1 : 0.01	104.63	40.42	37.2	3.22	59.58
1 : 0.2 : 0.01	105.46	49.67	45.26	4.41	50.33
1 : 0.3 : 0.01	105.47	52.41	48.41	4.0	47.59
1 : 0.4 : 0.01	105.2	53.76	50.22	3.56	46.24
1 : 0.5 : 0.01	104.96	53.93	51.65	2.28	46.07

Table 2. Content of Functional Groups in Coal and Products of Its Oxidation with Hydrogen Peroxide in the Presence of Oxalic Acid

Substance	Moisture%	Ash, %	Functional groups		
			COOH+OH, mEq/g	COOH, mEq/g	OH, mEq/g
Source coal	3.2	15.38	2.328	0.75	1.578
Oxidized coal	6.91	8.40	7.99	4.89	3.1
HA of the original coal	2.01	8.69	8.78	3.87	4.91
HA of oxidized coal	3.55	3.76	10.75	6.77	3.98
Residual coal of original coal	4.34	17.77	4.24	0.51	3.73

Residual coal of oxidized coal	4.81	19.89	1.78	0.87	0.91

In the next stage of the work, brown coal of the same composition was oxidized under optimal conditions, specifically with 10% H_2O_2 and 60% $H_2C_2O_4$, using a mass ratio of coal : H_2O_2 : $H_2C_2O_4$ = 1 : 0.1 : 0.01. The wet solid mass was then mixed with ground (0.25 mm) quicklime while continuously stirring until reaching a pH of 6-6.5. After adding the lime, stirring continued for 30 minutes. The resulting product consisted of irregularly shaped grains ranging from dark brown to black and had the following composition (wt.%): organic matter 68.6; total N 2.45; free humic acids 4.15; calcium humate 48.95.

The obtained meliorants were tested under laboratory conditions to determine the water retention capacity of soils influenced by humic meliorants. The water retention capacity, known as moisture capacity, is categorized into maximum adsorption capacity, field capacity, capillary capacity, and total moisture capacity. Maximum adsorption capacity is the maximum amount of tightly bound water held by sorption forces. Field capacity is the maximum amount of capillary water held after all gravitational water has drained. Capillary capacity depends on soil texture, structure, and density, typically ranging from 30-35% in well-structured heavy soils to 10-15% in sandy soils. Total moisture capacity is the maximum water a soil can hold when fully saturated, varying between 40-50%, and can increase to 80% or decrease to 30% under certain conditions.

Capillary moisture capacity was determined in the laboratory using a metal cylinder with a mesh bottom. A filter paper circle was placed at the bottom, and the soil was added while compacting it lightly. The height of the soil layer, cylinder diameter, and soil volume were measured. The cylinder was placed in a water bath so that the mesh bottom rested on the filter paper, allowing water to move into the soil. The cylinder was weighed daily until a constant mass was achieved, indicating complete capillary saturation. The capillary capacity was calculated using the formula:

$$K = \frac{(B - E)\cdot 100}{E}$$

where K = capillary capacity (%); V = mass of saturated soil in the cylinder (g); E = mass of dry soil in the cylinder (g).

Total moisture capacity was determined by placing the soil sample in the cylinder in a water bath, filling it with water to 1-2 cm above the soil, and leaving it for 24 hours. The cylinder was then covered tightly and inverted before being weighed. Total moisture capacity was calculated using the formula:

$$П = \frac{(a - в)\cdot 100}{в}$$

where a = mass of soil in the cylinder after water filling (g); b = mass of dry soil in the cylinder (g).

Table 3. Water Retention Capacity of Soils Influenced by Meliorant (%)

№	Sample number	Sampling location	Moisture capacity, % by weight		
			full	capillary	smallest
1	1	Control (soil without additions)	29,87	28,31	14,12
2			30,02	28,09	12,95
3			29,35	27,94	13,41
4			30,44	27,15	13,82
5			30,92	27,87	13,25
Ср.			30,12	27,94	13,97

6	2	Soil with ameliorant 10 t/ha	41,19	36,11	18,56
7			41,25	35,62	18,29
8			40,92	35,84	18,43
9			40,81	35,05	18,15
10			40,18	35,94	18,74
Cp.			40,38	34,74	18,45

The results of the tests are presented in Table 3. The data indicate that when soil is mixed with the meliorant obtained from oxidized coal at a rate of 10 tons per hectare, there are significant improvements in water retention capacity across the spectrum from total to minimum moisture capacity. Specifically, the untreated soil retains 30.12% at total moisture capacity, 27.94% at capillary capacity, and 13.97% at minimum moisture capacity. In contrast, the soil treated with the meliorant retains 40.38% at total moisture capacity, 34.74% at capillary capacity, and 18.45% at minimum moisture capacity.

Thus, the results of the conducted research convincingly demonstrate the potential to produce meliorants that absorb moisture and enhance soil structure based on oxidized brown coal using hydrogen peroxide in the presence of oxalic acid.

References

1. Aidarov I.P., Arent K.P., Golovanov A.I., et al. Concept of Land Melioration in Agriculture. MGI, Moscow, 1992.
2. Baishanova A.E., Kedelev B.Sh. Problems of Soil Degradation. Analysis of the Current State of Fertility in Irrigated Soils of the Republic of Kazakhstan // Scientific Review. Biological Sciences. – 2016. – No. 2 – pp. 5-13.
3. Litvinovich A.V., Hammam A.M., Lavrishchev A.V., Pavlova O.Yu. Meliorative Properties and Fertilizing Value of Different Size Fractions of Biochar (based on laboratory experiments) // Agrochemistry (Moscow). 2016. No. 9, – pp. 39-46.
4. Yukhnovets L.B., Kandelaki G.I. Cation Exchange Properties and Biological Activity of Humus-containing Meliorants for Reclamation of Saline Soils // Biological Sciences. – 1991, No. 10, – pp. 57-61.
5. Author's Certificate No. 1430389 USSR, cl. C05F 11/02. Method for Obtaining Soil Meliorant / Lishtvan I.I., Zhilko V.V., Abramets A.M., Dudarchik V.M., Zhishkevich M.M. – B.I. No. 38. 1988.
6. Author's Certificate No. 1781194 USSR, cl. C05F3/02. Meliorant for Soil Alkalization / Shok I.A., Ilyina T.N., Myasnikov N.F., Shakirov A.Sh., Alliluyev N.I., Vorona O.K. – B.I. No. 46. 1992.
7. Application No. 2135664 UK. IPC C05F 11/02. Composition for Soil Improvement / Evans, Silian Ivill – RZhKHIM 1985, 10L 243.
8. Application No. 59139788 Japan. IPC C09K 17/00. Organic Material for Soil Improvement and Its Use / Hirose Haryu, Otsuka Sadamu - RZhKHIM 1986, 5L 245.
9. Application No. 2649694 France. IPC C05G3/04. Composition for Soil Treatment and Method of Treatment Using This Composition / Vander Watt, Hendrik Van Heerden, Barnard Robin Oxley; Cronie Ivak Johannes, Dekker Johannes - RZhKHIM 1982, 5L 226.
10. Alexandrov I.V., Kossov I.I., Burkov P.A., Zhigmid D., Otgonboyar D. Humic Substances of Brown Coals as Meliorant for Saline Soils // Humic Substances in the Biosphere. – Moscow, Science, 1993, – pp. 174-177.

11. Kireycheva L.A., Glazunova I.V. New Organomineral Sorbent Meliorants for Detoxification of Soils Contaminated with Heavy Metals // Reports of the Russian Academy of Agricultural Sciences. – 1994, No. 4, – pp. 16-18.
12. Obukhovskaya T.D. Mercury Fixation by Humic Acid // Biological Sciences. – 1986, No. 7, – pp. 108-112.
13. Hristieva L.A., Azanov A.G., Tkachenko L.A. Influence of Soil Organic Matter and Fertilizers on Reducing Plant Damage Caused by Pesticides // Humic Fertilizers. Theory and Practice of Their Use. Part 4. – Dnepropetrovsk, 1973, – pp. 58-72.
14. Gorovaya A.I. The Role of Physiologically Active Humic Substances in Enhancing Plant Resistance to Pesticide Action // Biological Sciences. – 1988, No. 7, – pp. 5-16.
15. Yarchuk I.I., Bulgakova M.P. Physiologically Active Humic Substances as an Ecological Factor in Detoxifying Residual Herbicide Quantities // Biological Sciences. – 1991, No. 10, – pp. 75-80.
16. Kukharenko T.A. Methods for Determining the Content of Humic Acids in Solid Fuel Minerals // Chemistry and Technology of Fuels (Moscow), 1956. - No. 5. – pp. 32-43.
17. Danchenko N.N. Functional Composition of Humic Acids: Determination and Relationship with Reactive Ability // Candidate of Chemical Sciences Dissertation.- Moscow, – 1997. – pp. 109-110.
18. Tagayev I. et al. Analysis of the mineralogical composition of soil samples: Case study of Karmana district //E3S Web of Conferences. – EDP Sciences, 2023. – T. 434. – C. 03015.
19. Boynazarov B. et al. Production of bentonite and humus natural organic substances from fluoride compounds //E3S Web of Conferences. – EDP Sciences, 2023. – T. 377. – C. 03012.
20. Ganiev, P., Seytnazarov, A., Namazov, S., Usanbaev, N., & Temirov, U. (2022, June). Production of humic superphosphates based on central kizilkum phosphorites. In American Institute of Physics Conference Series (Vol. 2432, No. 1, p. 050037).
21. Umirov F., Urunova K., Temirov U. Study on wastewater treatment based on local minerals //E3S Web of Conferences. – EDP Sciences, 2023. – T. 377. – C. 03003.
22. Темиров У. Ш. и др. Особенности компостирования навоза крупного рогатого скота и фосфоритного шлама с добавкой фосфогипса //Universum: химия и биология. – 2018. – №. 8 (50). – С. 25-32.
23. Uktam T., Ahmed R., Shafoat N. Organ mineral fertilizer based on waste from livestock sector and low-grade Kyzylkum phosphorite //International scientific review. – 2016. – №. 5 (15). – С. 15-16.
24. Темиров У. Ш. и др. Гумификация органических веществ навоза при компостировании их с некондиционными фосфоритами //Universum: технические науки. – 2016. – №. 8 (29). – С. 1-5.
25. Azimova D. et al. Wastewater treatment using heat-treated defectate and MAP solution //IOP Conference Series: Earth and Environmental Science. – IOP Publishing, 2023. – T. 1142. – №. 1. – C. 012079.
26. Pirimov T. et al. Processing of serpentenites of the Arvaten deposit of Uzbekistan with the use of ammonium sulphate //E3S Web of Conferences. – EDP Sciences, 2023. – T. 402. – C. 14034.