Scaling up the Mechanochemical Technology for Producing Materials Enriched in Humic Acids

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Abstract. Mechanochemical treatment is widely used in industry as it allows one to reduce the number of processing stages, either reduce or completely eliminate the use of solvents, automate the technology and ensure its mobility. Energy input is an important parameter of mechanochemical treatment. In this study, the technology of mechanochemical oxidation of brown coal was scaled up using the planetary mills of AGO-2 and APF types, as well as K-7 and CEM-20 flow-type vibrocentrifugal mills. The technology of mechanochemical oxidation of brown coal makes it possible to increase the availability of humic acids in brown coal and the content of oxygen-bearing groups capable of complexation, as well as to improve sorption characteristics of the resulting product. Materials enriched in humic acids can be used as heavy metal sorbents in water bodies and as agents for soil amelioration. The rotor speed of 1400 rpm and the feed rates of 15 kg/h and 1.8 kg/h for CEM-20 and for K-7 vibrocentrifugal mills, respectively, are the optimal modes from the point of view of chemical and economic efficiency. These modes increase the yields of alkali-soluble and water-soluble humic acids from 23 to 59% and from <1 to 7%, respectively, which corresponds to the values reached using the laboratory-scale equipment.

1. Introduction
Humic acids are organic compounds that perform a number of functions in the biosphere, including the accumulative, transport, regulatory, protective, and other ones. Brown coal is one of the most important sources of humic acids. The world's brown coal reserves are estimated at billions of tons, with a significant portion being located in Russia. However, brown coal is poorly suited for use as a fuel because of its low calorific value and susceptibility to spontaneous combustion during transportation. Producing humic acids and humin-containing products from brown coal is a good alternative to its application as an energy source. The mechanochemical techniques make it possible to conduct solid-phase chemical reactions, thereby avoiding the use of solvents and increasing environmental friendliness and economical efficiency of the processes [1, 2]. Such advantages as the reduced number of processing stages and the mobility of mechanochemical activators make it possible to treat brown coal and brown coal waste directly on-site, which also solves the problems related to its transportation.

From the perspective of solid-state chemistry, brown coal is an interesting object for mechanochemical modification to change its chemical properties. Solid-phase treatment of brown coal with alkalies, which enhances the extractability of humic acids due to the formation of sodium humate via the acid–base mechanism, has been best studied. It has recently been found that mechanochemical treatment of brown coal in a laboratory-scale planetary-type activator in the presence of sodium percarbonate is accompanied by oxidation of the organic matter in brown coal and increases the content...
of phenolic and carboxyl groups in humic acids [3, 4]. Due to the high content of complexing groups, humic acids are rather promising substances for designing heavy metal sorbents, which can be used at natural environment sites [5]. A large number of reviews focused on determining the composition, structure simulation, and physicochemical properties of humic acids have been published. There also are publications devoted to binding of humic acids to organic and inorganic substances, as well as the methods for their modification [6].

The solid-phase methods for treatment and modification of humic acids within the humin-containing feedstock, including the mechanochemical ones, are currently used rather commonly in technology but remain insufficiently studied. Simultaneously, the research into mechanochemical reactions of humic acids typically focuses on laboratory-scale mechanochemical activators.

A laboratory ball mill and a planetary activator have been most widely described in the literature. These types of equipment are ideal for laboratory-scale experiments. The processes occurring inside the reactors and the exposure type have been carefully studied and simulated many times. The results of mechanical activation using these devices are well reproduced. However, only several dozen grams of a sample can be activated in a planetary mill per cycle. In order to develop the technology of mechanochemical modification of brown coal humic acids to produce heavy metal sorbents at a marketable volume, the processes under study need to be scaled up [7] using the flow-type mechanochemical equipment that has a similar type of mechanical impact.

The goal of this study was to determine the optimal conditions for mechanochemical treatment of brown coal in industrial-scale mills, which would allow one to attain the effects obtained in laboratory mills for larger-scale production of materials (heavy metal sorbents and ameliorants) enriched in humic acids.

2. Materials and Methods

Brown coal (alkali-soluble humic acids, 23.6 ± 0.4 %; ash, 10.7 ± 0.3 %) from the Itatskoe deposit was used in this study. The contents of alkali-extractable and water-soluble humic acids in all samples were determined in compliance with the International Standard ISO 5073:2013 (Brown Coals and Lignites – Determination of Humic Acids).

The first stage of technology scale-up was conducted using an APF water-cooled planetary-type mechanochemical activator equipped with two jars with steel grinding balls 8 mm in diameter (the total weight of the grinding bodies, 900 g; the weight of loaded substance, 100 g). Grinding body acceleration at an instant when it was detached from the grinding chamber walls was 200 m/s²; the duration of mechanical treatment was 2 min. The treatment conditions matched those for the laboratory-scale equipment: 5 wt.% sodium percarbonate additive; moisture content in the mixture, 3.5%. The maximum power consumption of the activator was 6 kW; the output was 6 kg/h.

The second scale-up stage was conducted using a K-7 flow-type vibrocentrifugal mill (Novits OJSC, Novosibirsk, Russia) with the output of 10 kg/h and the maximum power consumption of 2.2 kW. The rotor speed was varied from 420 to 1400 rpm. The mill was equipped with two cylindrical grinding bodies: the reagents were supplied through a feeder on one side, and the finished product was collected in a receiving hopper on the other side. The diameter and the operating length of a grinding body were 40 and 400 mm, respectively. The grinding bodies were steel balls 5 mm in diameter. The weight of the balls in a working body was 2600 g. The treatment conditions matched those for the laboratory-scale equipment: 5 wt.% sodium percarbonate additive; moisture content in the mixture, 3.5%.

The third scale-up stage was performed on a CEM-20 flow-type vibrocentrifugal mill, with the maximum output of 50 kg/h and the maximum power consumption of 2.2 kW.

In the experiments, cadmium(II), chromium(III), cobalt(II), and lead(II) ions were sorbed from solutions based on Tris-HCl buffer (pH 8.0); the concentration of each metal in the solution was 20 mg/kg for the first experimental series and 100 mg/kg for the second experimental series. An accurately weighed portion of the sorbent (1 mg sorbent per ml of the solution) was added. The mixture was thermostated at T = 25°C and shaking frequency of 130 min⁻¹. Samples to determine the residual content of heavy metals were collected every hour, as well as at an instant when the sorbent was added. The residual content of heavy metals in the solution was determined by ICP-AES using a solution containing 0.5 m/l Sc(III) ions as an internal standard.
Evaluation of the effect of growth promoters on plants in field tests involved three stages: (1) setting up an experiment; (2) field observations and survey; and (3) laboratory analysis plant samples. A section of median traffic strip of a major highway in Novosibirsk (Russia) was selected as a test object. The 3 m wide grassplot is located between two lanes of the highway, on a slope being ~ 15° steep. The experiment was set up manually in four replicas; the plot length was 4 m; the area of the entire test ground was 204 m². The test grounds of the same size without the product added to the soil were used as controls (five replicas).

3. Results and Discussion

The technology discussed in this paper consists in conducting solid-phase oxidation of the organic matter in brown coal in the presence of sodium percarbonate [3, 4, 8]. It was shown in the experiments performed using an AGO-2 laboratory-scale planetary-type activator that the optimal processing conditions were as follows: 5 wt.% sodium percarbonate additive; moisture content in the reaction mixture, < 12–13 %; exposure duration, 2 min; grinding body acceleration at an instant when they were detached from the jar walls, 20 g. Under these conditions it is possible to increase the content of alkali-soluble humic acids to 70 ± 3 %, and the content of water-soluble humic acids from <1 % to 15 ± 1 %. The resulting product has an increased content of phenolic and carboxyl groups and better sorption characteristics compared to the original coal [9].

Proper equipment was selected at the first stage of technology scale-up. A review of the current market of semi-industrial mechanical activators was performed. The market segment of semi-industrial mechanochemical equipment (with the output of ~ 50 kg/h) included centrifugal elliptical ball mills (Novits OJSC, Novosibirsk, Russia; Xinxiang Unitfine Machinery Co., Ltd., China), jet mills (New technologies, St. Petersburg, Russia), finger disintegrator mills (Prodselmash OJSC, Novosibirsk, Russia; Desintegraator Tootmise, Estonia). It is worth mentioning that only the vibrocentrifugal mills can be used to perform a mechanochemical reaction (a prerequisite is that the grinding body has a simultaneous mechanical impact on the entire reagent mixture rather than on separate reagent particles).

At the first stage of scale-up, the mixture of brown coal and sodium percarbonate was treated in an APF planetary ball mill. The results obtained using the APF activator under conditions matching those used during treatment in an AGO-2 laboratory-scale activator (grinding body acceleration at an instant of detachment from the jar wall, 20 g; treatment duration, 2 min; moisture content, 3.5%) are well reproduced. The yields of alkali-soluble and water-soluble humic acids were increased to 65 ± 3% and 12 ± 1 %, respectively. The maximum output of the APF activator is 6 kg/h.

Although the maximum power consumption of this equipment is 6 kW, the actual power consumption with loaded jars does not exceed 3 kW. Unfortunately, this type of mechanochemical equipment is not flow-through. It requires careful maintenance by service personnel, as well as the time-consuming procedures of jar loading and unloading. So operation of this equipment is accompanied by high energy expenditure.

Table 1 summarizes the results of the second stage of mechanochemical technology scale-up, which was conducted using flow-type vibrocentrifugal equipment. The yield of water-soluble humic acids as an indicator of treatment efficiency was studied. The consumption of sodium percarbonate Na₂CO₃ × 1.5H₂O₂ was estimated according to pH of the product suspension in distilled water.

### Table 1. The results of mechanochemical treatment of brown coal in the presence of sodium percarbonate in a K-7 flow-type vibrocentrifugal mill

| Rotor speed (rpm) | Yield of water-soluble humic acids (%) | pH  |
|-------------------|---------------------------------------|-----|
| 0                 | < 1%                                   | 10  |
| 420               | < 1%                                   | 9.5 |
| 560               | 3.2 ± 0.1                              | 8.5 |
| 840               | 3.6 ± 0.1                              | 6.6 |
| 1120              | 5.8 ± 0.2                              | 6.3 |
| 1400              | 6.8 ± 0.2                              | 6.5 |
The pH values listed in Table 1 demonstrate that no mechanochemical reaction occurs between brown coal and sodium percarbonate at frequencies < 560 rpm, since sodium percarbonate is not consumed, remains in the final mixture, and increases pH. Since pH of the treatment product suspension for the samples obtained in the rotor speed range of 840–1400 rpm is not overestimated, it is fair to say that percarbonate was consumed and the samples obtained at these frequencies are the products of a mechanochemical reaction between the organic substance of coal and sodium percarbonate. When scaling up the technology of oxidative treatment of brown coal performed using the semi-industrial scale equipment, we managed to increase the extractability of water-soluble humic acids from 1 to 7 %.

A pilot-scale batch (100 kg) was produced, with the CEM-20 industrial vibrocentrifugal mill (output, 50 kg/h; rotor speed, 1400 rpm) used at the stage of mechanical activation. The pH of the aqueous suspension of the product (1:10) is 6.5; the yield of water-soluble humic acids is 7.5 ± 0.3 %; the yield of alkali-soluble humic acids is 55 ± 2 %, being indicative that the organic matter of brown coal has been successfully oxidized with sodium percarbonate using the industrial-scale mechanochemical equipment. The resulting product was tested as a heavy metal sorbent under the laboratory and field conditions, as well as a soil ameliorant along a major highway in Novosibirsk.

Laboratory testing of the product as a sorbent. In order to assess the efficiency of brown coal subjected to mechanochemical modification in the presence of sodium percarbonate as a heavy metal sorbent, experiments focused on sorption from solutions containing a mixture of trace elements were conducted. Humic acid samples were added to a solution containing cadmium, chromium, cobalt, and lead ions (20 mg/l of each metal in the first experiment; ~ 100 mg/l in the second experiment). In all the cases, metal concentrations decreased dramatically after the first 30 minutes of product exposure to the mixture. One can see that the mechanochemically produced sorbent removed most of heavy metals from the solution due to sorption.

Table 2. The results of sorption of a metal mixture onto the products of mechanochemical activation of brown coal

| Metal | C₀(Me) (mg/l) | Cₚₚ(Me) (mg/l) |
|-------|---------------|----------------|
| Pb²⁺  | 130 ± 20      | 3.2 ± 0.4      | 0.69 ± 0.08 |
| Co³⁺  | 74 ± 8        | 1.1 ± 0.1      | 0.21 ± 0.02 |
| Cr³⁺  | 100 ± 10      | 1.4 ± 0.2      | 0.16 ± 0.02 |
| Cd²⁺  | 90 ± 10       | 10.0 ± 0.9     | 3.5 ± 0.4   |

Thus, brown coal mechanochemically oxidized using the scaled-up technology in the flow-type vibrocentrifugal mill efficiently removes heavy metals from the solution containing a mixture of trace elements (Cd²⁺, Cr³⁺, Co³⁺, and Pb²⁺). The residual concentrations of heavy metals in the solution are significantly lower than those in the control experiments, where the untreated brown coal was used as a sorbent. The product was also tested in field experiments on heavy metal sorption from the water area of the Novosibirsk reservoir [10]. It was applied onto a highly porous polymer matrix that ensured all the necessary performance characteristics: easy collection and regeneration and the possibility of its flow-through use. It was shown that the product could be used for removing Cd (II), Cu (II), Pb (II), and Zn (II) ions from a natural reservoir and was highly efficient.

Experiments were carried out to study the impact of adding the mechanochemically oxidized brown coal to the soil on the grassplot of the median strip of the Kamenskaya Highway in Novosibirsk. Table 3 lists the results of determining the state of the herbaceous cover by the end of the growing season. The percentage of soil surface covered with grass (the projective cover of grass stand) along the margins of the control plots was ≤ 30% and ranged from 60 to 80% across the experiment replicas. In variant 2, where 10 g/m² of the product was added, grass covered 70–80% of the soil. The results were similar in variant 3, where 30 g/m² of the product was added. In variant 4, where 10 g/m² of the product and a
fertilizer were added and gramineous plants were undersown, the projective cover of grass stand was 80%.

**Table 3.** The average projective cover of grass stand on the test plot (% of the total soil area)

| Variant                                           | Total projective cover of grass stand | Including gramineous plants | Including weeds and motley grasses |
|---------------------------------------------------|--------------------------------------|----------------------------|-----------------------------------|
| 1. Control                                        | 68                                   | 38                         | 30                                |
| 2. Product being added (10 g/m²)                  | 75*                                  | 40                         | 35*                               |
| 3. Product being added, 30 g/m²                   | 78*                                  | 48*                        | 30                                |
| 4. Product being added (10 g/m²) + N₁₂₀P₀₆₀K₆₀ + seeding | 82*                                  | 50*                        | 32                                |

*The difference with the control is reliable at the 95% level

The observed trend towards increasing projective cover of grass stand was accompanied by an increase in the gramineous component on experimental plots nos. 3 and 4 by 10% and 12%, respectively, compared to the control plot. The results of determining the height and productivity of grass stand on the experimental plot are presented in Table 4. Addition of the product significantly increased grass height and weight on the experimental plots compared to the control one. Undersowing of gramineous grasses did not lead to significant predominance of the gramineous component. The effect of the product increased with its dose. Fertilization and undersowing of gramineous grasses contributed to the increase in grass height and weight.

**Table 4.** Height and productivity of the grass stand on the experimental plot

| Variant                                           | Average height (cm) | Productivity (g/m²) (abs. dry) |
|---------------------------------------------------|---------------------|-------------------------------|
| 1. Control                                        | 12.8                | 94.8                          |
| 2. Product being added (10 g/m²)                  | 14.4                | 114.0*                        |
| 3. Product being added (30 g/m²)                  | 18.2*               | 117.6*                        |
| 4. Product being added (10 g/m²) + N₁₂₀P₀₆₀K₆₀ + seeding | 22.8*               | 120.8*                        |

*The difference with the control is reliable at the 95% level

Hence, the material produced using the semi-industrial flow-type vibrocentrifugal mill was efficient in the experiments on grass remediation on soil plots exposed to significant anthropogenic load. The treated plot is characterized by higher coverage, average grass height and weight, and a higher percentage of gramineous components compared to the control plot.

4. Summary

Proper equipment for scaling-up of the mechanochemical technology of brown coal oxidation has been selected. Three stages of scaling-up of mechanochemical technology of brown coal oxidation were used: from the larger-size equipment of the same type as that used in the laboratory-scale technology, to the semi-industrial-scale flow-type mechanochemical activator. The optimal technological modes of mechanical treatment of brown coal in a vibrocentrifugal mill giving rise to a product with elevated contents of water- and alkali-extractable humic acids were determined. The rotor speed of 1400 rpm and the feed rate of 15 kg/h and 1.8 kg/h for the CEM-20 for K-7 vibrocentrifugal mills, respectively, are the optimal modes from the point of view of chemical and economic efficiency. These modes increase the yields of alkali-soluble and water-soluble humic acids from 23 to 59 % and from <1 to 7%, respectively, which corresponds to the values reached using the laboratory-scale technology.
5. References

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