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Scaling of the mechano-chemical process of production of silicon chelates from plant raw materials

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In order to scale up the mechanochemical process of production of biologically active silicon chelates from plant raw materials the transfer from laboratory mechanochemical reactors to industrial equipment with a productivity of 15-70 kg / h was carried out. The efficiency of raw material grinding (by size characteristics of the product) and activation effects (by solubility of silicon dioxide) were studied depending on the technological treatment regimes (processing intensity and feed rate). The characteristics of the product obtained at laboratory scale (equilibrium concentration of soluble silicon chelates of 28 mg / l) were improved with a rotor speed of 1500 rpm and a productivity of 15-20 kg / h. Taking into account the energy costs, the rotation speed of 1200 rpm and feed rate of 43 kg / h can be considered as the optimal mode, which provides the obtaining of product with an equilibrium concentration of soluble chelates of 24 mg / l.

Keywords: Scaling, Mechanochemistry, Mechanochemical reactor, Technology, Silicon chelate

INTRODUCTION

Silicon performs a number of important functions in the human body, animals and plants [1]. The highest biological activity is displayed by complexes of silicon with organic compounds [2]. Rice husk is a promising renewable source of biogenic silicon dioxide with a content of up to 20% by weight. The chemical form of silicon in the rice husk is hydroxylated amorphous silica. It concentrates at the outer surfaces of plant tissues, where it forms a cellulose-silica composite membrane [3]. Due to its unique composition and fibrillary ultrastructure rice husk has high-strength characteristics, chemical inertness, low density and high ash content. Thereby the tasks of efficient mechanical and mechanochemical processing of silicon dioxide in plant raw materials are closely related to the increase of the specific surface area, the production of chemically active surface centers, and the synthesis of soluble products. Thus, it was snown in [4, 5] on model systems (silica gel and pyrocatechol, silica gel and dihydroquercetin, silica gel and green tea catechins) at a laboratory scale that the interaction of silicon dioxide with polyphenolic compounds can be achieved using a solid-phase mechanochemical method. Hydroxyl groups of polyphenols interact with the silanol groups of silicon dioxide during the mechanochemical treatment of the reagents, which leads to the formation of surface complexes of silicon with polyphenols. With subsequent dissolution, the silicon chelates go into solution.

The introduction of developments in the industry requires scaling of the dependencies obtained on laboratory equipment and the establishment of optimal technological regimes [6].

Therefore, the goal of this work was to determine the optimum conditions for mechanochemical treatment of silicon-containing plant raw material in industrial mills, allowing achieving the effects obtained in laboratory mills for the production of biologically active products with an increased amount of water-soluble silicon.

MATERIALS AND METHODS

The following materials and chemicals were used: rice husk *Oryza sativa (L.)* (Liman sort, Krasnodar Krai, Russia), green tea *Camelia sinensis (L.)* (State standard # TU 9191-003-00570186-04, Krasnodar Krai, Russia)**,** $(NH_4)_2MoO_4$ (99.5 %, Russia), H_2SO_4 (99.9 %, Russia), Na_2SiO_3 (99 %, Russia), KBr (optical grade, Russia), pyrocatechol (99 %, Alfa Aesar), ammonium acetate (98 %, Russia), ascorbic acid (99 %, Russia), oxalic acid (99 %, Russia).

Moisture content of the samples of plant raw materials and products was measured according to [7] using an automatic moisture analyzer Radwag WPS 50SX (Poland) and was equal to 5.8-6.1 %. Granulometric analysis was carried out on a vibrating screen “Analysette-3 Pro”, equipped with a set of screens 20-1000 μm (FRITSCH, Germany). The specific surface area of the samples was determined from the thermal desorption of nitrogen on the “Sorbtometer M” instrument (Katakon, Russia) using Gregg and Singh approximation [8].

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Mechanochemical treatment of plant raw material

Mechanochemical treatment of plant raw material was carried out in an industrial mechanochemical reactor of centrifugal roller type mill "RM-50" (production of ISSC SB RAS, Novosibirsk), equipped with water cooling [9]. A mixture of 85% rice husk containing silica, and 15% green tea containing catechins was used as a raw material for the production of chelated silicon. The grinding bodies were steel rollers fixed on the drive shafts which treated mechanically the material with a controlled intensity. The technological regimes used in the work were: feed rate 15-70 kg / h, rotor speed 900-1500 rpm. The temperature in the treatment zone was controlled by a water-cooled jacket and did not exceed 65-70 ° C.

Determination of the equilibrium concentration of silicon chelates in solution

The equilibrium concentration of silicon chelates in solution was determined according to the following procedure. Samples were dissolved in 0.05 M acetate buffer under a hydromodule of 1000 at 25 ° C for 4 h with periodic mixing. After dissolution, the suspension was centrifuged to separate the supernatant (5000 rpm, 15 min. A 350 μl portion of supernatant was taken into a 5-ml test tube, then 150 μl of a solution of ammonium molybdate (0.5 M) was added and allowed to stay for 10 min at room temperature. Then, 300 μl of a reducing agent solution (0.4 M ascorbic acid and 0.7 M oxalic acid) and 3.25 ml of water were added. After 30 min, the optical density was mwasured at a wavelength of 810 nm. The concentration of silicon chelates was determined from a calibration curve plotted using a State Standard Sample of silica # 8934-2008) under similar conditions.

RESULTS AND DISCUSSION

Comparison of apparatuses with different types of mechanical action was conducted under laboratory conditions [10]. It was shown that the use of machines with shear type of action, such as centrifugal roller mill, is preferable for the solid-phase reaction between silicon dioxide of rice husk and polyphenols in the matrix of plant raw materials. Using this type of equipment provides reducing of the particle size and increasing the specific surface area from 0.5 to 2.3 m^2/g, disordering of the ultrastructure of cell walls, amorphization of cellulose and activation of silicon dioxide surface with formation of new active centers. For this reason, a centrifugal roller mill RM-50 was chosen for scaling. It can provide a capacity of up to 100 kg of product per hour, which is sufficient for the industrial production of silicon chelates.

The most important technological parameters that determine the efficiency of processing of raw materials in the mechanochemical reactor are the rotor speed and the fillability of the processing zone associated with the feed rate. Often with the same particle size of the raw material, the fineness of product grinding is proportional to the power consumption. The processing of the rice husk mixture with green tea was carried out with two variable parameters: the input frequency of the current and the feed rate. The input frequency of the current determines the rotor speed and reactor power consumption (Table 1).

Fig. 1 shows a typical particle size distribution of the processed product at a fixed rotor speed. It can be seen that a decrease in the feed rate of the raw material through the treatment zone causes a decrease of material passing per the unit of time. Thereby more energy is supplied to the raw material (per unit mass) and the grinding proceeds more efficiently.

Increasing of the efficiency of grinding can be achieved not only by reducing the feed rate, but also by increasing the energy input. Summary data on the influence of processing parameters on the average particle size of the rice husk are presented in Table 2. As can be seen from the results in Table 2, the most efficient grinding occurs with low raw material feed rate and high rotor speed, the feed rate being more important. Thus, acceptable regimes providing efficient grinding, high yields of the product at relatively low power consumption are as follows: rotor speed of 1200-1350 rpm and feed rate of 30-40 kg / h. In particular, for the sample obtained at 1200 rpm and 33 kg / h, the specific surface area was equal to 2.1 m^2 / g, which is comparable to the value for the sample obtained at laboratory scale [9].

Determination of the equilibrium concentration of soluble chelated forms of silicon and consideration of the data in Table 2 in graphic form (Fig. 2) allows determination of the maximum attainable concentration of chelated forms of silicon, as well as the specific change in concentration with increasing energy intensity (by how many units will the chelate concentration increase with an increase in the engine rotation speed by 1 rpm or a decrease in the feed rate by 1 kg / h).

The maximum attainable concentration of chelated forms of silicon, corresponding to a rotation speed of 1500 rpm and supply of raw

materials tending to zero, is 40.2 mg/l. For the rotation speeds of 1200 and 900 rpm, these values are 29.5 and 18.5 mg / l, respectively. It can also be noted that under intensive mechanical action (1500 rpm), the dependence of the concentration of monomeric forms of silicon on the feed rate, determined from the slope of the straight line, is stronger than under less impact (1200 and 900 rpm).

Table 1. Dependence of the rotor speed and power consumption of the mechanochemical reactor on the input current frequency.

Current frequency, Hz	Rotor speed, rpm	Energy consumption without raw materials, kW	Energy consumption with raw materials, kW
20	550	2.7	5.0
30	900	5.5	7.1
40	1200	9.5	10.3
50	1500	14.5	18.7

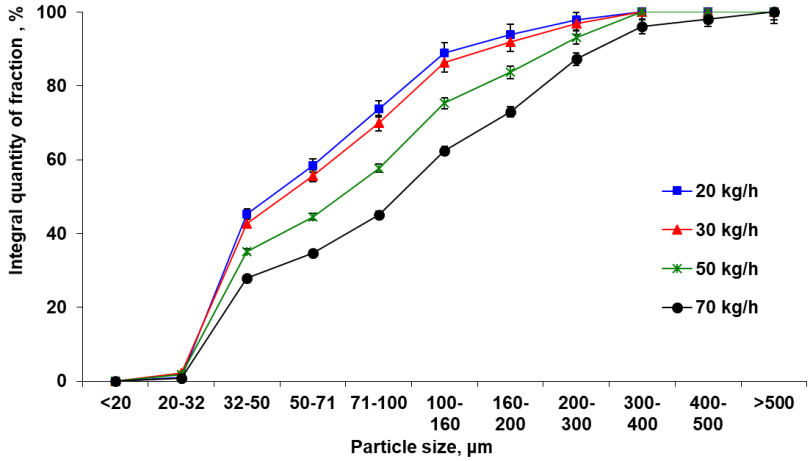

Figure 1. Influence of feed rate on the granulometric composition of mechanically activated rice husk (at a rotor speed of 1200 rpm)

Table 2. Dependence of the average particle size of the product on the rotor speed and feed rate

Rotor speed, rpm	Feed rate, kg / h	Average particle size of the product, μm
900	15	145 ± 2
	20	157 ± 1
	33	172 ± 3
	43	179 ± 4
	52	170± 3
	70	199 ± 3
1200	15	92 ± 5
	20	84 ± 1
	33	92 ± 2
	43	107 ± 6
	52	112 ± 6
	70	119 ± 3
1350	15	62 ± 2
	20	69 ± 4
	33	73 ± 3
	43	91 ± 2
	52	94 ± 2
	70	104 ± 3
1500	15	57 ± 3
	20	57 ± 2
	33	62 ± 2
	43	73 ± 2
	52	76 ± 1
	70	80 ± 3

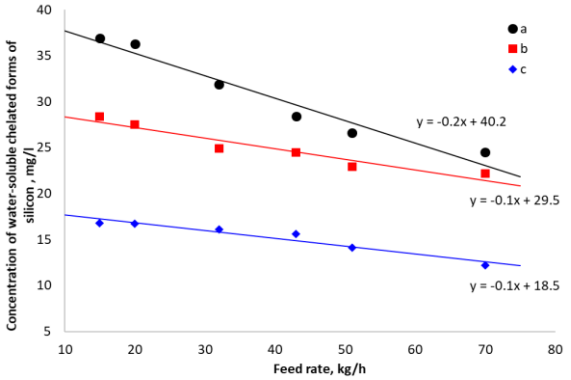

Figure 2. Dependence of the equilibrium concentration of water-soluble chelated forms of silicon on the conditions of mechanochemical treatment: a, b, c: 1500, 1200, 900 rpm, respectively.

Taking into account the energy costs and the minimum angle of slope (indicating a more stable mode of treatment) the optimum mode is as follows: rotor speed of 1200 rpm and feed rate of 43 kg / h, which leads to a product with an equilibrium concentration of soluble chelates of 24 mg / l.

CONCLUSIONS

On the basis of the presented results it can be concluded that the intensity of the mechanical action and the feed rate of raw materials play a significant role on the efficiency of mechanochemical interactions in the activation of the raw materials. Optimal technological regimes of mechanical treatment of plant raw materials in a semi-industrial centrifugal roller mill leading to the production of a product characterized by an increased concentration of chelated soluble forms of silicon were determined. The most rational modes from the point of view of chemical and economic efficiency are: rotor speed of 1200 rpm and feed rate of 43 kg / h. This mode provides an increase in the yield of chelated forms of silicon from 6 to 24 mg / l, which corresponds to the values reached at laboratory level.

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ОКРУПНЯВАНЕ НА МЕХАНОХИМИЧНИЯ ПРОЦЕС НА ПРОИЗВОДСТВО НА СИЛИЦИЕВИ ХЕЛАТИ ОТ РАСТИТЕЛНИ СУРОВИНИ

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(Резюме)

За укрупняване на механохимичния процес на производство на биологично-активни силициеви хелати от растителни суровини е направен преход от лабораторни механохимични реактори към промишлено оборудване с производителност от 15-70 kg / h. Ефективността на смилане на суровината (оценена от размерите на продукта) и на активиращите ефекти (оценени от разтворимостта на силициевия диоксид) са изследвани в зависимост от технологичните режими на обработка (интензивност на обработката и скорост на захранване). Характеристиките на лабораторно получения продукт (равновесна концентрация на разтворими силициеви хелати от 28 mg / l) са подобрени с използване на скорост на ротора от 1500 rpm и производителност от 15-20 kg / h. Вземайки под внимание енергийните разходи, като оптимални могат да се считат скоростта на въртене от 1200 rpm и скоростта на захранване от 43 kg / h, които осигуряват получаването на продукт с равновесна концентрация на разтворими хелати от 24 mg / l.