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CHARACTERISTICS OF SILICON DIOXIDE PRODUCED FROM RICE HUSK

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Abstract

A demanding problem of today's chemical technology is synthesis of high-purity amorphous silicon dioxide with a high specific surface area from raw materials of plant origin. From the point of view of energy saving, an optimal method for obtaining silicon oxide from rice husk is the one which involves its chemical purification followed by heat treatment. The paper has shown that the use of the double extraction method makes it possible to achieve high-quality characteristics of the synthesized silicon dioxide. It has been found that the rice husk treatment with an alcoholic solution of hydrochloric acid, followed by treatment with an aqueous solution of sulfuric acid, leads to removal of metal ions and a significant amount of lignin and cellulose from the raw material. Silicon dioxide, obtained after 5-minute firing of the prepared raw material at 600°C, is a white powder with a particle size of 0.9 to 10 µm and specific surface of 235–250 m²/g. The product is X-ray amorphous and of high purity. The high-quality characteristics of silicon dioxide synthesized by the proposed method opens up good prospects for its use as a carrier for active masses of catalysts, pharmaceutical and cosmetic preparations.

Keywords: silicon dioxide, rice husk, double extraction, characteristics, morphology, structure

ХАРАКТЕРИСТИКА ДІОКСИДУ КРЕМНІЮ, ОТРИМАНОГО З РИСОВОГО ЛУШПИННЯ

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Анотація

Актуальним завданням сучасної хімічної технології є синтез високочистого аморфного діоксиду кремнію з високою питомою поверхнею із сировини рослинного походження. Оптимальним, з погляду енергозбереження, є спосіб отримання оксиду кремнію з рисового лушпиння, що передбачає її хімічну очистку з подальшою термообробкою. У цій роботі показано, що використання методу подвійної екстракції дозволяє досягти високих характеристик синтезованого діоксиду кремнію. Встановлено, що обробка рисового лушпиння спиртовим розчином хлоридної кислоти з подальшою обробкою водним розчином сульфатної кислоти призводить до очищення сировини від іонів металів та значної кількості лігніну та целюлози. Силіцій (IV) оксид, отриманий в результаті 5-тихвилинного випалу підготовленої сировини при 600 °С, є порошком білого кольору з розміром частинок від 0.9 до 10 мкм і питомою поверхнею 235–250 м²/г. Продукт є рентгеноаморфним та високочистим. Високі характеристики діоксиду кремнію, синтезованого запропонованим способом, відкривають великі перспективи його використання в якості носія для активних мас каталізаторів, лікарських та косметичних препаратів.

Ключові слова: силіцій (IV) оксид, рисове лушпиння, подвійна екстракція, характеристика, морфологія, структура

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Introduction

High-purity silicon dioxide with an amorphous crystallographic structure is a valuable raw material for the production of high-tech equipment, ceramic and chemical products, and for pharmaceutical industry and bioengineering. It is used in the synthesis of high-purity silicon, which is the basis of up-to-date electronics and solar panel photocells [1; 2]. Structural materials of polymeric and ceramic nature, catalyst carriers, and membranes are manufactured using silicon dioxide [3–8]. The product with a purity of more than 95 % is a wide-spread component of building mixtures, cements and concretes [4]. It is also in demand as a filler and thickener in the pulp and paper industry and paint and varnish industry, as well as in the production of detergents [2; 4; 6; 9]. Oxide dispersions are used in suspension electrolytes for deposition of composite metal coatings [10; 11]. Given the high adsorption capacity, amorphous silicon dioxide with an extended specific surface is of interest when considering it as a carrier in medications, an adsorbent in wastewater purifiers, or an additive to activated carbons and cosmetic compositions [2; 6; 12–14].

The traditional method for obtaining amorphous silicon dioxide from mineral raw materials is energy-consuming and environmentally unsafe [5]. An alternative way to obtain this product is processing of rice production waste which contains a significant amount of SiO_2. A large number of scientific papers in this field point to good prospects for the synthesis of amorphous silicon dioxide from this kind of raw material [15]. The cheapness of rice husk, combined with a rather economical technology for its processing [16], arouse considerable interest of the scientific community and grant givers to finding optimal ways to obtain high-purity silicon dioxide from rice husk.

Removal of metal ions from rice husk is carried out by acid treatment of the natural raw material [17]. In [16], the effectiveness of acid treatment of rice husk with 2 M hydrochloric acid solution was compared with the method of removal of metallic impurities from the husk by mixing them with citric acid under heating. It was shown that the latter method ensures a basic substance content of 98.67 % of the silicon dioxide obtained, while the use of hydrochloric acid provides for the purity of the product at the level of 95.6%. In addition to acid treatment, this process chain included heat treatment [16; 18] and dissolution of solid combustion products in an alkaline solution. The final stage of this process is the precipitation of SiO_2 upon acidification of the resulting solution [16–20].

Another method for obtaining pure silicon dioxide from rice husk is as follows: prior to heat treatment, the raw material is subjected to acid treatment in order to remove metal and carbon containing impurities [8]. In [21], in order to remove metal ion impurities from rice husk, it was proposed to carry out a chemical pre-treatment of the plant raw material with solutions of 0.4 M hydrochloric or 0.2 M sulfuric acids. Subsequent heat treatment at 540 °C leads to the formation of pure amorphous silicon dioxide. It was proposed to carry out preliminary removal of lignin and cellulose from rice husk with hydrochloric acid solutions in ethanol [22] and sulfuric acid solution [23], respectively.

Elaborate purification of raw materials of plant origin from impurities, such as metal ions, lignin, and cellulose, is possible using the double extraction method [24]. The method involves two successive chemical treatments of the raw material prior to heat treatment. At the first stage, metal ions and lignin are removed in a hydrochloric acid solution in ethanol. The subsequent removal of cellulose is carried out in an aqueous solution of sulfuric acid. This method of purifying rice husk prior to heat treatment makes it possible to remove the carbon containing components from the raw material to the maximum, which significantly increases the purity of the final product.

The purpose of this study is to identify the main characteristics of silicon dioxide obtained from rice husk using chemical purification by double extraction [24].

Methods

The chemical composition of rice husk before and after double extraction was found by IR spectroscopy in the frequency range of ν = 800–3500 cm^{-1} using a Specord M – 80 IR spectrometer and by displacement chromatography using a CHNS/O 2400 Seriesll analyzer.

X-ray diffraction patterns of silicon dioxide were obtained using a DRON 3.0 diffractometer under CuKα radiation. The interplanar spacing on the x-ray diffraction patterns of the samples were compared with the data from the ASTM (American Society for Testing and Materials) file cabinet.

The surface morphology of rice husk ash and its elemental composition were studied using a REMMA 102-02 scanning electron microscope

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(Ukraine) with an energy-dispersive X-ray spectrometer.

The specific surface of the powders was determined by the BET method based on the volumes of gas previously adsorbed on the surface of the analyzed sample from the working gas mixture flow (nitrogen-helium) at liquid nitrogen temperature and then desorbed from it under a temperature increase.

The calculation of the relative content of particles of each fraction was carried out according to the formula:

$N_i = n_i / \sum n_i \cdot 100\%$,

where n_i is the number of particles of the same particle size fraction (δ_i, μm),

$\sum n_i$ is the total number of counted particles.

Results and discussion

Rice husk contains silicon, metal ion impurities, and carbon containing components, such as lignin and cellulose. The carbon content of the feedstock causes carbon contamination of the silicon dioxide obtained after the heat treatment of rice husk. Carbon containing contaminants can be removed by extracting the organic components. It should be noted that this process can be carried out in a controlled manner, and it allows a strictly specified amount of carbon containing components to be extracted. Based on the data given in [24], the maximum removal of the organic components of rice husk is achieved in the process of double extraction, with the removal of lignin in a solution of 1.5% hydrochloric acid in 96% ethanol at 80 °C for 6 hours and subsequent removal of cellulose in 15% aqueous solution of sulfuric acid at 100 °C for 6 hours.

Spectroscopic studies of the raw rice husk showed the presence of the following chemical bonds (Fig. 1): O–H (ν=3100 – 3450 cm^{-1}); C–H (ν=2930 – 3000 cm^{-1}); C≡C (ν=2300 – 2450 cm^{-1}); C–C (ν=1590–1660 cm^{-1}); C–O (ν=1310–1490 cm^{-1}) and Si–O; Si–O–Si; Si–O–C (ν=850 – 1300 cm^{-1}).

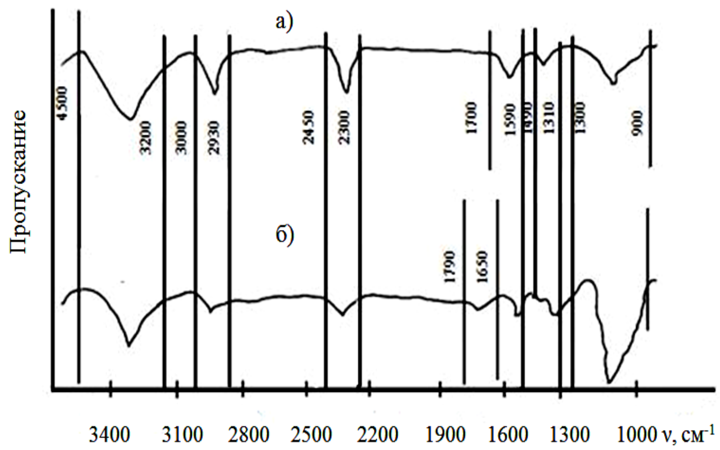


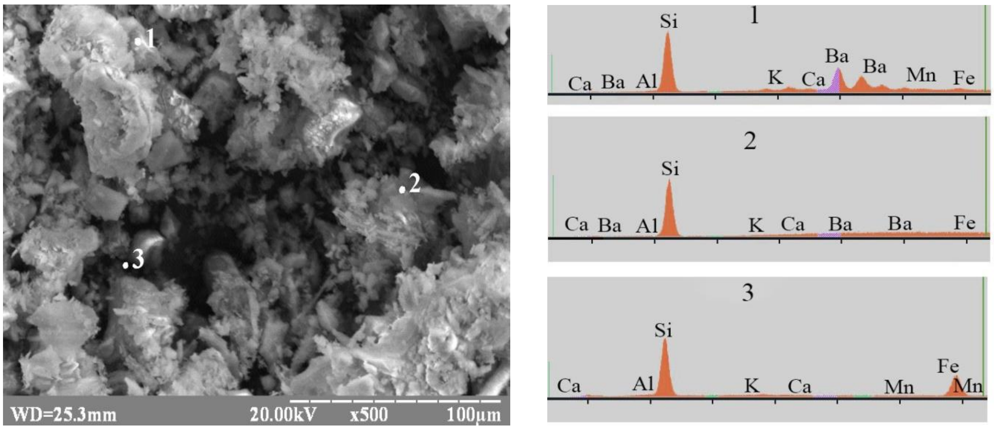
Fig.1 IR – spectra of rice husk: a) initial sample; b) sample after double extraction of carbon containing components

Absorption bands in the ranges of ν=2930–3000 cm^{-1} and ν = 2300–2450 cm^{-1} are characteristic of chemical bonds present in lignin. The ranges ν = 1590–1660 cm^{-1} and ν=1310–1490 cm^{-1} are to be attributed to the chemical bonds of the cellulose structure.

The spectral response characteristic corresponding to the rice husk sample subjected to the double extraction treatment indicates a significant attenuation of the intensity of the above peaks. Reducing the amount of carbon containing components naturally leads to an increase in the relative content of silicon dioxide. This effect illustrates the difference in the magnitude of the peaks, corresponding to the initial and acid-treated rice husk, in the frequency range of ν = 850–1300 cm^{-1} (Fig. 1). The proposed method of processing the raw material of natural origin reduces the carbon content of it from the initial 35.51 (% wt.) to 11.88 (% wt.).

Thus, the purification of rice husk by the double extraction method allows a maximum efficient removal of carbon containing components. In addition, this kind of purification ensures removal of metal ions present in the plant raw material. The corresponding data were obtained in the study of the products of calcination of the raw and purified rice husk. Heat treatment of unpurified rice husk was carried out at a temperature of 600 °C for 30 minutes.

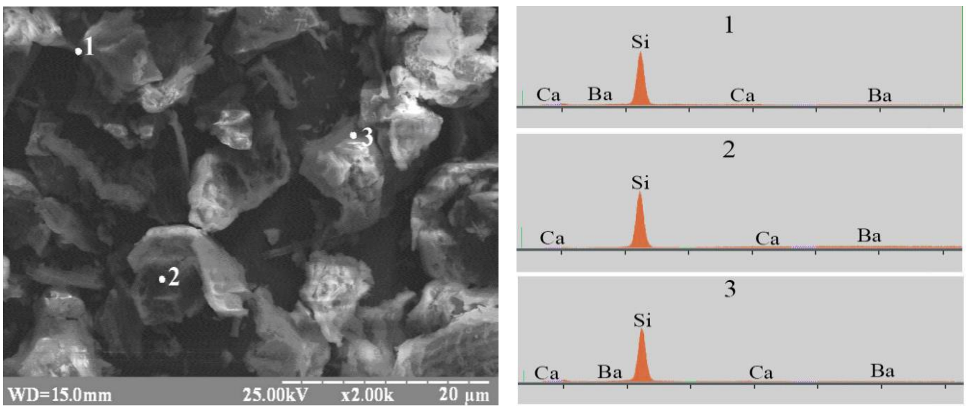
Fig. 2 shows that the ash resulting from the calcination of rice husk is flakes with no definite shape, assembled in agglomerates of variable size. Energy-dispersive analysis of the elemental composition of rice husk ash in different areas of the surface detected the compounds of metals, such as iron, barium, manganese, and aluminum, present in the sample composition.



а *б*

Fig. 2 Micrograph of the surface of rice husk ash (a) and energy dispersive spectra (b) obtained in different areas of the surface

Rice husk subjected to double extraction treatment is largely free from carbon containing components. In this case, the initial structure of lignin and cellulose fibers is disturbed and, apparently, the surface accessible for air oxygen oxidation during the combustion process significantly increases. This is indicated by the fact that the complete combustion of the organic component of the raw rice husk at 600 °C is achieved after 6 hours, while the 5-minute heat treatment is sufficient for the raw material after its preliminary purification. The latter allows a complete removal of carbon containing components of the rice husk and obtaining high-purity silicon dioxide free from soot residues. The surface morphology of the ash obtained in this way differs from the morphology of the ash obtained from the initial raw material. Fig. 3 shows rather well-defined flakes of silicon dioxide of about the same sizes and of no definite shapes. Energy dispersive analysis of the elemental composition of this sample showed that the content of metal compounds is negligible. Thus, acid extraction ensures removal of metal compound impurities from rice husk, which increases the purity of the initial raw material for obtaining high-purity silicon dioxide.



а *б*

Fig. 3 Micrograph of the surface of silicon dioxide synthesized from purified rice husk (a) and energy dispersive spectra (b) obtained in different areas of the surface

X-ray phase studies of silicon dioxide obtained by calcination of rice husk indicate the amorphous nature of the crystallographic structure of the sample (Fig. 4).

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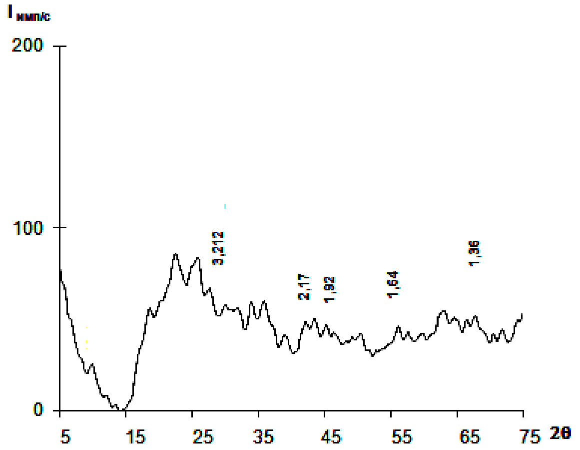

Fig. 4 X-ray diffraction pattern of a sample of silicon dioxide obtained from the raw rice husk

A diffraction pattern of silicon dioxide synthesized from purified rice husk has a similar appearance (Fig. 5). Therefore, heat treatment at the level of 600 °C makes it possible to obtain amorphous silicon dioxide from both the raw and treated rice husk. Therefore, the specified temperature condition is satisfactory for the calcination of the raw material under study.

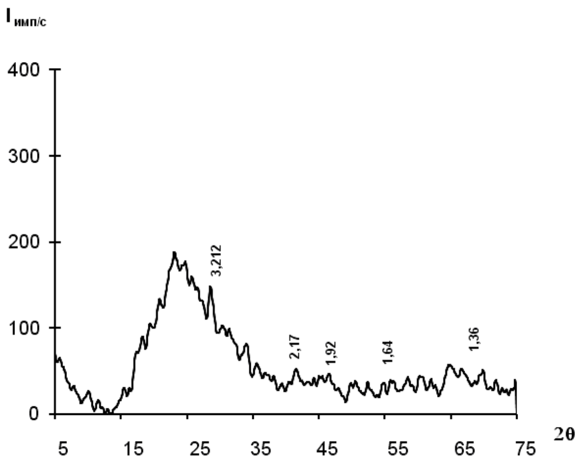

Fig. 5 X-ray diffraction pattern of a silica sample obtained from purified rice husk

Characteristics of silicon dioxide obtained from the raw and purified rice husk are presented in Table 1. The so-called technical silicon dioxide is contaminated with metal oxides and soot, which is reflected in its appearance. Silicon dioxide powder obtained by calcination of unpurified rice husk is gray in color. The specific surface area of technical silicon dioxide does not exceed 135 m²/g. The scope of such silicon dioxide is very limited. Despite the amorphous structure, its disadvantages, such as low specific surface area, contamination with impurities and unsatisfactory appearance, narrow its scope to fillers in non-critical products of the ceramic and polymer industry.

Table 1

Properties of silicon dioxide powders obtained from rice husk

Characteristics	Technical silicon dioxide	Silicon dioxide obtained from purified rice husk
Appearance	Gray powder	White powder
Mass fraction of moisture, %	1.2 – 1.5	0.9 – 1.2
Water extract pH	6.8 – 7.0	6.5 – 6.8
Specific surface by BET method, m²/g	120 – 135	235 – 250

Silicon dioxide obtained from double-extracted rice husk is a white powder with a purity of 99.9 %, free from metal and carbon impurities, with a high specific surface area approaching 250 m² / g.

The assessment of the fractional content of silicon dioxide particles in the powder obtained from purified rice husk was carried out by counting the particles of various sizes recorded on a micrograph. The maximum value of the overall dimensions of particles δi was used as a controlled geometric parameter. Fig. 6 shows that the particle sizes of silicon dioxide range from 0.8 to 100 μm. Note that the largest percentage of (N) falls on particles that have a size of 1 to 10 microns.

Thus, disperse analysis of silicon dioxide particles obtained from purified rice husk showed that the proposed method for processing plant raw materials makes it possible to synthesize a microscopic powder with the most represented particle fraction of about 2 μm.

Conclusion

1. The study of the morphology and chemical composition of the products of thermal destruction of the raw and purified rice husk showed the high efficiency of the double extraction method in the synthesis of high-purity silicon dioxide powder of microscopic dimensions. It has been found that the successive purification of rice husk from metal ions and carbon containing components in solutions of 1.5 % hydrochloric acid in 96 % ethyl alcohol and 15 % aqueous sulfuric acid solution ensures almost complete removal of metal impurities and a significant amount of lignin and cellulose. The latter allows heat treatment of an extremely short duration, not exceeding 5 minutes.

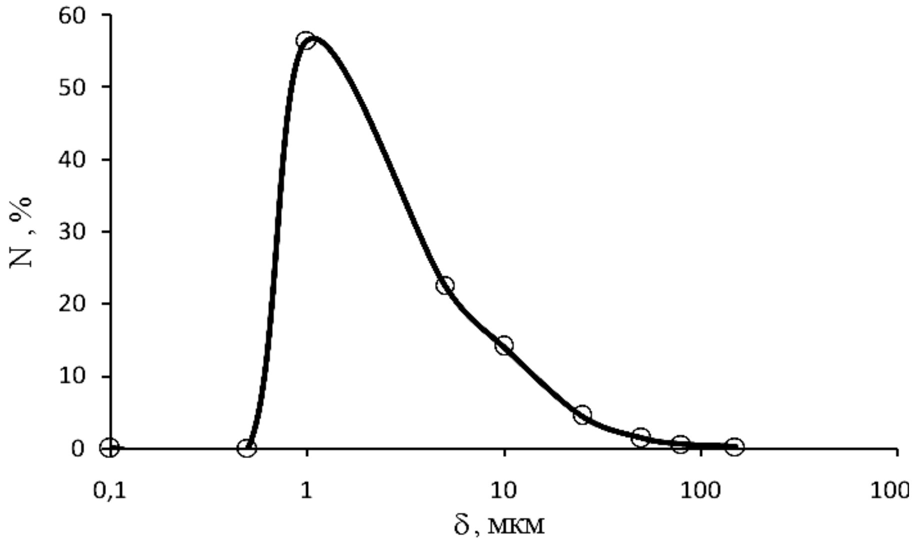

Fig. 6 Fractional content of silicon dioxide particles

2. Assessment of the main characteristics of the silicon dioxide powder obtained from the purified rice husk shows that the purity of the product is 99.9 %. Silicon dioxide is a white powder with the most probable particle size of about 2 µm. Silicon dioxide is characterized by an amorphous structure and high specific surface area of about 250 m²/g. The obtained characteristics offer good prospects for the use of such silicon dioxide in the chemical and pharmaceutical industries as a carrier of active components.

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