Dependence of Porosity of Amorphous Silicon Dioxide Prepared from Rice Straw on Plant Variety

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Contents of silica and extractive substances in rice straw depending on rice varieties were investigated. The samples of amorphous silica were prepared, their microelement composition and morphology were investigated, and the values of true and bulk density were estimated. The porous structure of the samples was studied by the Brunauer-Emmett-Teller (BET) method and by water vapour sorption; the specific surface values, as well as the pore diameter and volume, were also determined. Sorption properties of the SiO_2 surface were analyzed on a sample of Mn^{2+}-ions and the organic dyes brilliant green and methylene blue.

Keywords: Rice straw; Silica; Porous structure; Sorption properties

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INTRODUCTION

In the process of rice (*Oryza sativa* L.) cultivation, 1 to 2 kg of straw is generated for every kilogram of rice grain harvested. The main components of straw are cellulose, hemicelluloses, lignin, silica, and phenol fractions. Because rice straw (RS) is a cheap, renewable raw material, it is widely used in the production of cellulose and building materials, as a fertilizer, and as an addition to cattle feed (Sergienko *et al.* 2004). However, the use of RS has some restrictions. High cellulose and silica contents exclude it from being used in a daily animal diet in a large amount. For the same reason, RS decays slowly, which makes it difficult to use as a fertilizer. As a result, a considerable amount of straw is burnt in the fields. In prospective, straw may serve as an alternative energy source: it may be burnt in special furnaces for generation of thermal and electric power, or subjected to biological processing for obtaining biofuel. The RS ash consists primarily of amorphous silicon dioxide, which has a highly extended surface and may be used as a multi-purpose, highly efficient sorbent.

Because of the necessity of using RS as a valuable, large-tonnage, renewable raw material, investigation of variations of its composition for different varieties of rice has become topical. The work in this area indicates how considerable the differences are between the varieties (Bainton *et al.* 1991; Vadiveloo 1995; Agbagla-Dohnani *et al.* 2003; Sun 2010; Ghasemi *et al.* 2013). The chemical composition of straw depends on the variety of rice and conditions of its cultivation.

The aim of this work consisted of studying the effect of rice varieties on physico-chemical properties of amorphous silica produced from rice straw.

EXPERIMENTAL

Materials

Straw of some Far-East rice varieties, *i.e.*, Khankaiskii 429, Priozernyi 61, Darii 23, Rassvet, Dolinnyi, Lugovoy, Darii 8, and Khankaiskii 52 (harvest of 2010; Timiryazevskii settlement, Primorskii kray) served as the subject of investigation.

Methods

For extraction of soluble organic and inorganic substances from rice straw, a weighed amount of the raw material was put into a heat-resistant glass jar, and then water or 0.1 N hydrochloric acid, was added in the ratio of 1:13 solid:liquid (in some experiments, 1:22). The mixture was heated at 80 to 90 °C for 1 h. The extract was filtered out through blue ribbon filter paper.

The samples of amorphous silica were prepared from rice straw using the following procedure. Some straw was reduced to fragments of 10 to 50 mm in length, washed with water, and dried in air. Then, after it was weighed, it was treated with 0.1 N hydrochloric acid at 90 °C for 1 h, washed with water on a filter, dried in air, burnt to ash at 300 °C for removal of volatile substances, and calcinated in a muffle furnace in air at 600 to 700 °C to a constant mass.

The samples were identified by the IR spectroscopy (Shimadzu FTIR Prestige-21 Fourier-spectrophotometer, Japan; frequency range 400 to 4000 cm^{-1}, Vaseline oil), X-ray diffraction (Bruker D8 ADVANCE diffractometer, Germany; Cu K_{α}-radiation), and thermogravimetric (MOM Q-1000 thermoanalytical system, Hungary; heating rate 5° per min, air) methods, using standard techniques (Zemnukhova *et al.* 2005; Zemnukhova *et al.* 2006).

The elemental composition was determined by using the inductively coupled plasma mass-spectrometry method with a JCP-MS Elan DRC II apparatus (Perkin-Elmer, USA), according to the standard technique. The micrographs of the samples were obtained using a Hitachi S5500 high-resolution scanning electron microscope (Japan).

The specific surface (S_{sp}) values and pore size distribution were estimated with nitrogen adsorption, using an ASAP 2020 analyzer (Micrometrics Instrument Corporation, USA). The S_{sp} values were calculated by using the Brunauer-Emmett-Teller (BET) method, based on the nitrogen adsorption isotherms and the pore distribution by the Barret, Joyner, Halenda (BJH) method. The S_{sp} values for silica were also determined by the water vapour adsorption measured under isopiestic conditions at 25 °C. The specific surface was estimated for the capillary condensation area. The efficient pore diameters were found using the differential curves of pore volume distribution, taking into account the sizes obtained from the water vapour adsorption-desorption isotherms.

Adsorbability of the samples was characterized by adsorptive capacity relative to the two organic dyes: a basic thiazine dye (methylene blue) and an aniline dye (brilliant green). The technique is described in detail in Zemnukhova *et al.* (2014b).

The experiment on manganese ion sorption was carried out under static conditions, and the Mn^{2+} concentration ranged from 5 to 60 mg/L. The sorbent was kept in solution for 24 h; it was found earlier that this amount of time was sufficient for

equilibrum (Sheveleva *et al.* 2009). The Mn^{2+} concentration in solution was estimated by the atomic absorption method, with a AA-770 spectrophotometer (Nippon, Jarrell Ash, Japan) in the acetylene-air flame.

RESULTS AND DISCUSSION

It has been described (Kharchenko *et al.* 2008) that aqueous and acid extracts of plant raw material, rice production waste among them, have an inhibitory effect on steel corrosion because of the presence of high-molecular weight organic compounds. The aqueous extract of rice hull was shown to inhibit St. 3 steel corrosion by 54%, while the acid extract inhibited corrosion by 94.9%. In connection with the importance of the task of metal protection from corrosion, in this work, the content of extractive substances in straw of different varieties of rice was determined (Table 1). It was found that water extracted soluble substances were in the quantity of 2.47 to 5.50%, while 0.1 N HCl extracted substances were 4.52 to 7.25%. In both cases, the minimum amount of soluble substances was extracted from the straw of the Khankaiskii 429 variety (No. 1 in Table 1). The amount of extractive substances depends on the ratio of the solid and liquid phases in the extraction process; in the course of the experiment the maximal value, 18%, was achieved at the ratio solid:liquid of 1:22. Since the acid solution extracts more soluble substances from RS, calcination of the latter after acid treatment results in obtaining much more pure silica (93.36 to 97.86%) than after treatment with water (89.60 to 92.34%) (Zemnukhova *et al.* 2005). Only the stage of extraction of soluble substances has the right conditions for the purity and the properties of amorphous silica. Varying extraction conditions (low ratio solid:liquid, high acidity of medium, or repeated acid treatment) can be achieved at 99.84% purity of SiO_2 prepared from RS. Moreover, high purity of the product is not always important, and the presence of carbon as an impurity in silica may have a positive influence on the sorption properties of the material (Sheveleva *et al.* 2009).

Table 1. Extractive Substances in Rice Straw

No.	Variety of plant	Extractive substances (%)	
		H_2O	HCl
1	Khankaiskii 429	2.47	4.52
2	Priozernyi 61	5.45	7.25
3	Darii 23	5.21	5.21
4	Rassvet	5.50	5.53
5	Dolinnyi	3.10	7.00
6	Lugovoy	5.00	6.85
7	Khankaiskii 52	3.25	3.03
8	Darii 8*****	18.3	23.3
9	Chemical $SiO_2 \cdot nH_2O$ GOST 4214-78	0	0

(0.1 N HCl, ratio Solid:Liquid = 1:13
***** ratio Solid:Liquid = 1:22

It is known from literature (Abou-El-Enin *et al.* 1999; Zemnukhova *et al.* 2005; Wang *et al.* 2006; Ghasemi *et al.* 2013) that various varieties of rice differ considerably

by the straw composition, which includes 40 to 69% of cellulose, 34 to 43% of hemicelluloses, and about 4 to 14% of lignin. The average amount of ash equals 6.7 to 24.8% (Wang *et al.* 2006). Differences in the straw composition are not connected directly with the parentage of varieties and cannot be used in rice breeding programs (Abou-El-Enin *et al.* 1999). The ash content in RS for *Primorskii krai* equals 11.5 to 13.5% (Table 2). That is comparable with that of rice cultivated in the USA and Middle East (10.3 to 17.7%).

Table 2. Characteristics of Amorphous Silica Samples Prepared from Rice Straw

No.	Ash content (%)	SiO_2 content (%)	H_2O content (%)	SiO_2 density true/bulk (g/cm^3)	Parameters of porous structure		Sorption capacity (mg/g) BG/MB
					S_{sp} (m^2/g) BET/water	Average diameter (nm) BET/water	
1	13.5	91.9	<0.1	2.14/0.570	11/41	52.7/7.5	61.8/117.1
2	12.5	97.5	<0.1	2.12/0.542	35/64	19.2/7.8	ND/162.3
3	11.5	91.9	<0.1	2.06/0.505	47/84	9.9/6.0	90.8/169.0
4	13.5	86.9	<0.1	2.19/0.604	9/50	85.7/6.6	ND/145.0
5	13.5	92.1	<0.1	2.07/0.487	31/75	ND/6.4	126.5/191.8
6	11.5	93.6	<0.1	2.10/0.531	33/22	19.6/10.3	112.2/170.6
7	13.5	90.9	<0.1	2.16/0.542	26/ND	33.5/ND	72.3/168.2
8	12.3	97.5	<0.1	2.02/0.500	102/ND	6.9/ND	ND
9		88.4	11.6	2.15/0.663	73/81	ND/1.6	30.0/124.9

ND - not determined

The silica content in rice straw is somewhat less than that in rice hull (Zemnukhova *et al.* 2005; 2006). Thus, the ash yield for straw varies in the range 6 to 14%, while it ranges from 9 to 12% for hull. In addition, the silica yield is influenced by the type of treatment. In the framework of this work, the straw was preliminarily treated with hydrochloric acid, which resulted in a lower yield of the dry residue after calcination. However, silica prepared this way was considerably more pure (93.36 to 97.86%) than silica formed after the incineration of RS without acid treatment (86.54 to 88.16%), because a large share of impurities was removed with acid.

Finding small amounts of water, less 0.1%, is a peculiarity of silica prepared from RS (Table 2), while silica from rice hull never contains less than 0.5% of water.

According to Zemnukhova *et al.* (2005; 2006), silica from RS contains much more aluminium and iron than silica prepared from hull (2.8 and 6.7 times, respectively). Concentrations of other impurities (Na, Mg, Ca, Zn, Mn) in the samples from straw are close to those from hull (Zemnukhova *et al.* 2005; 2006). In the present work, the elemental compositions of the prepared silica samples are given (Table 3). No essential differences between varieties of rice were revealed (the content of most of the elements in different varieties differs no more than 1.2 to 1.3 times). It was established that the highest concentrations typical for elements such as potassium (4.83 to 6.35 mg/g), calcium (2.91 to 3.72 mg/g), magnesium (2.00 to 2.35 mg/g), phosphorus (1.20 to 1.29 mg/g), and manganese (1.00 to 1.23 mg/g) were comparable with the literature data (Abou-El-Enin *et al.* 1999; Zemnukhova *et al.* 2005). The samples also contained iron (522 to 666 μg/g), sodium (304 to 432 μg/g), zinc (179 to 193 μg/g), and barium (131 to

134 μg/g). Titanium, strontium, boron, copper, nickel, lead, and cobalt were detected in concentrations less than 100 μg/g (Table 3).

Table 3. Elemental Composition of Silica Samples Prepared from Straw of Rassvet (No. 4 in Table 1) and Dolinnyi (No. 5 in Table 1) Varieties (μg/g)

Elements	Rice variety	
	Rassvet	Dolinnyi
K	6351.43	4830.13
Ca	3718.80	2912.19
Mg	2353.70	2001.73
P	1291.56	1201.49
Mn	1232.54	1003.96
Fe	666.22	572.12
Na	432.72	304.77
Zn	192.73	179.41
Ba	130.77	134.41
Ti	96.90	71.78
Sr	33.88	32.52
B	19.67	14.71
Cu	12.92	10.87
Ni	8.38	1.11
Pb	4.92	2.24
Co	1.86	1.47

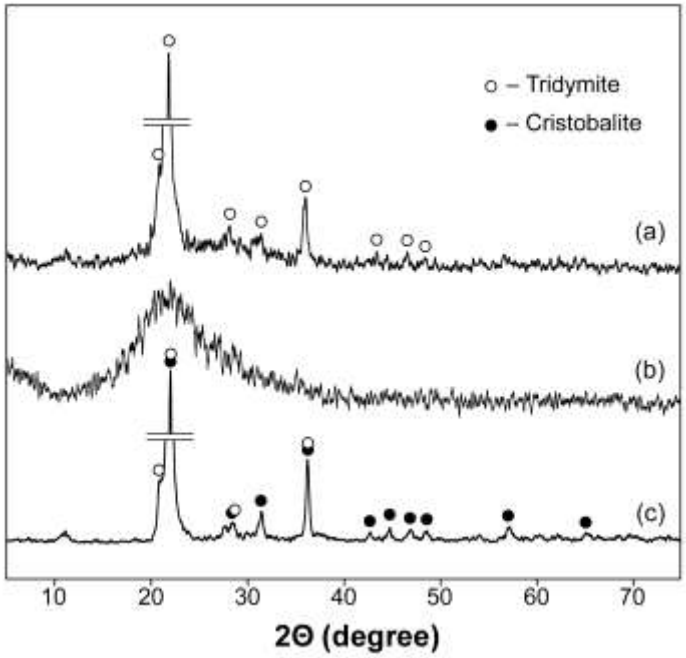

Fig. 1. X-ray diffraction patterns of amorphous SiO_2: (a) Prepared by calcination of untreated RS at 600 °C; (b) prepared by calcination of RS preliminary treated with 0.1 N HCl, at 600 °C; and (c) prepared by calcination of sample 2 at 1000 °C

All the silica samples were found to be X-ray amorphous (Fig. 1); the X-ray diffraction patterns exhibited one wide maximum, which is typical for amorphous structures in the range $2\theta \approx 22°$. Calcination above 800 °C resulted in the crystallization of silicon dioxide as either a tridimite or as a mixture of tridimite and crystobalite, depending on the amount of impurities. It is known that the degree of crystallization of biogenic silica depends, to a great extent, on both the calcination temperature and the content of impurities (in particular K^+), which can catalyze the fusion of silicon dioxide (Wang *et al.* 2012).

The typical IR spectrum of amorphous silica prepared from rice straw (No. 4 in Table 2) is presented in Fig. 2b, in comparison with that of the commercial sample GOST 4214-78 (Fig. 2a, No. 9 in Table 2). Both of the spectra contain the absorption bands at 467, 799, and 1093 to 1099 cm^{-1} related to the valent and deformation vibrations of Si–O–Si siloxane bonds present in amorphous silicon dioxide (Zemnukhova *et al.* 2014b). The spectrum of the commercial $SiO_2 \cdot nH_2O$ (Fig. 2a) has the bands at 3400 to 3431 and 1630 to 1638 cm^{-1}, related to the valent and deformation vibrations of O–H bonds. The absorption band at ~958 cm^{-1} is indicative of the presence of the Si–OH silanol bond. Absence of such bonds in the IR absorption spectrum of the silica sample prepared from RS (Fig. 2b) correlates with the small amount of water content in this sample (Table 2).

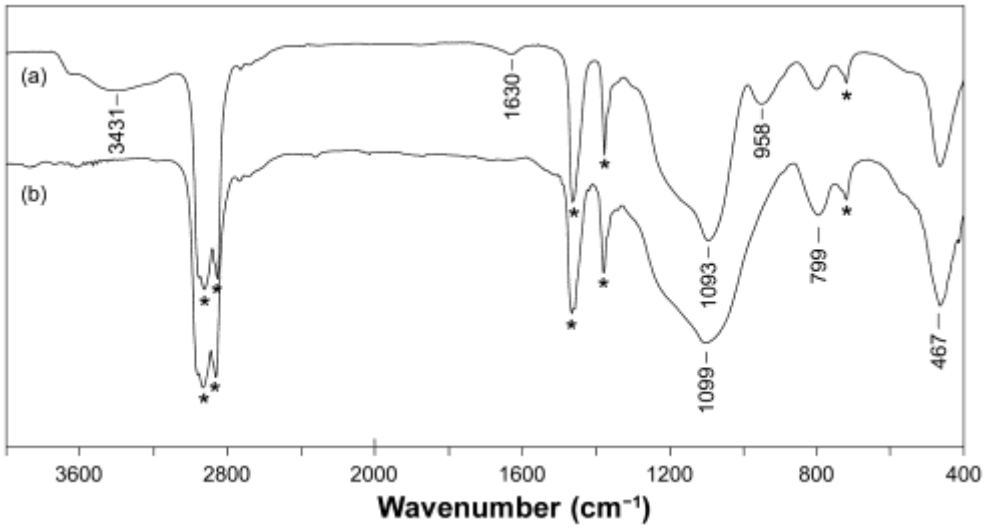

Fig. 2. IR absorption spectra of amorphous silica samples: (a) Commercial $SiO_2 \cdot nH_2O$ GOST 4214-78 (No. 9 in Table 2); and (b) SiO_2 from Rassvet variety rice straw (No. 4 in Table 2).
* denotes absorption bands of Vaseline oil

The thermal investigation of the sample obtained from the Darii-8 variety (No. 8 in Table 1) showed that heating the straw resulted in the removal of unbound water when the temperature was over 150 °C, and its amount equaled 7.8%. Subsequent heating caused decomposition of the organic compounds, which proceeded up to 570 °C, and the mass of the solid residue equaled 12% from that of the initial sample.

One can see from the micrographs obtained, by means of a scanning electron microscope (Fig. 3), that the calcinated silica of biogenic origin partially maintained the structure of the plant tissues, and its particles were about 1 mm in size (Fig. 3a). However, such fragments were porous and had an extended surface due to burning-out of

organic substances from straw. It can also be seen that the surface of silica was formed by 10- to 20-nm particles separated by a developed network of channels and pores (Fig. 3b).

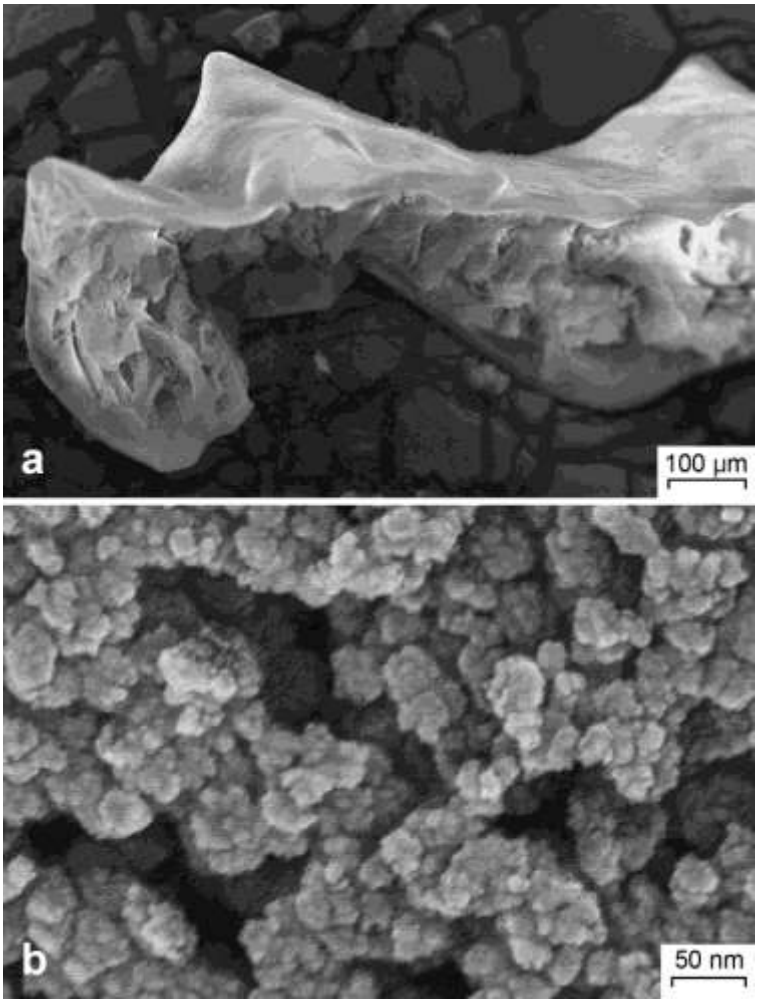

Fig. 3. Microphotographs of amorphous silicon dioxide prepared from straw of Dolinnyi variety, at (a) low and (b) high magnification

Investigation of the porous structure of the amorphous silica samples, using the water vapour absorption method, showed that the samples prepared from rice straw had a biporous structure with a wide pore distribution and two predominant diameters (Fig. 4).

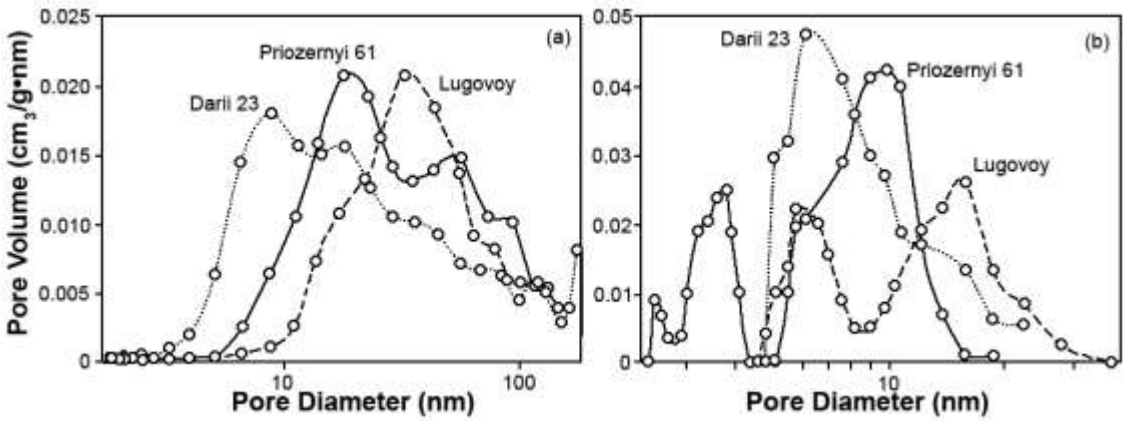

Fig. 4. Pore volume distribution in amorphous silicon dioxide samples obtained from different rice varieties according to data on sorption of (a) nitrogen and (b) water vapour

Moreover, silica prepared the same way from rice hull was monoporous with a more narrow pore size distribution (Zemnukhova *et al.* 2010). The nitrogen sorption data demonstrated that the average pore diameter varied within the range of 6.9 to 85.7 nm, while the specific surface value estimated by the BET method was 8.6 to 102.4 m^2/g, depending on the variety of rice (Table 2, Fig. 5).

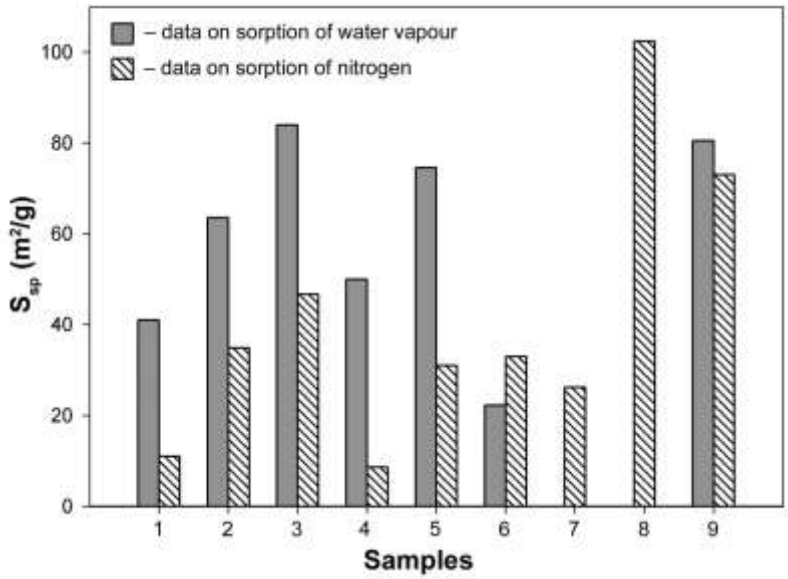

Fig. 5. Variety dependence of specific surface for amorphous silica samples from RS (numbers according to Table 2)

Because of its high specific surface value and developed porous structure, amorphous silica of plant origin can be used as a sorbent. During the last few years, the sorption properties of the products of rice production waste processing have been actively investigated (Ahmaruzzaman and Gupta 2011). It is known that amorphous silica from RS efficiently sorbs bacteria (Zemnukhova *et al.* 2014a). Among the samples prepared

the same way, silica from RS has a higher sorbability to *E. c*oli and *B. subtilis* than that prepared from rice hull (Zemnukhova *et al.* 2014a).

The present work also included the investigation of metal ion sorption. Figure 6 demonstrates the isotherm of Mn^{2+} ion sorption on amorphous silica prepared from straw of the Dolinnyi variety (Fig. 6, curve a), in comparison with mineral-origin silicon dioxide GOST 4214-78 (Fig. 6, curve b). As it can be seen, plant silica exhibited a much higher sorption capacity than the mineral one (7.8 and 3.6 mg/g, respectively).

Sorption capacity of the samples relative to the two organic dyes, methylene blue, and brilliant green, equaled 117.1 to 191.8 and 61.8 to 112.2 mg/g, respectively. It should be noted that the difference in sorption capacity of silica in relation to various compounds is also connected with the number of hydroxylic groups on the SiO_2 surface causing its acid-basic properties. In this case, one can observe a certain correlation with the results of sorption measurements on nitrogen and water vapour. Thus, sample 1 (Table 2) had a comparatively low sorption capacity to the dyes and was characterized by a low specific surface value, while samples 3 and 5 had a higher sorption capacity and a more extended surface.

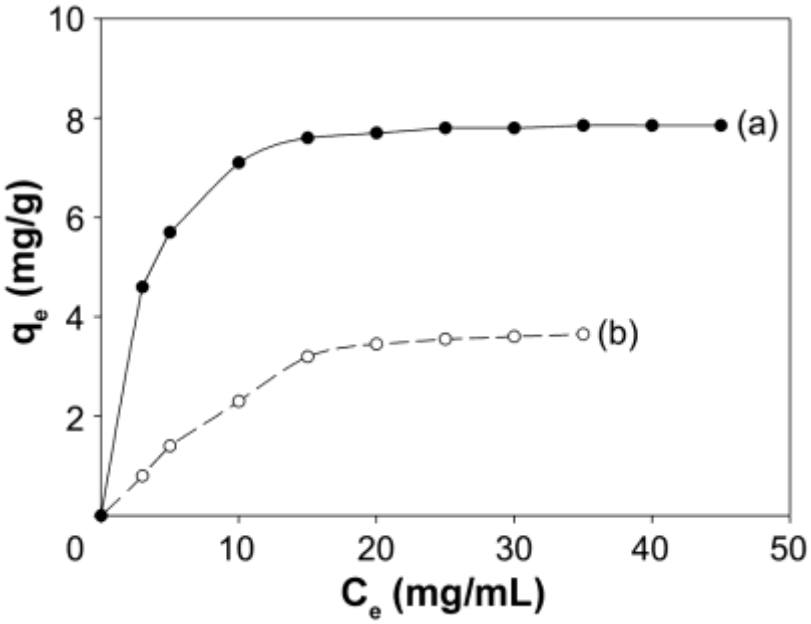

Fig. 6. Sorption isotherm of Mn^{2+} ions on amorphous silica samples: (a) SiO_2 from RS of Dolinnyi variety (No. 5 in Table 2); and (b) $SiO_2 \cdot nH_2O$ GOST 4214-78 (No. 9 in Table 2)

CONCLUSIONS

1. The content of silica in the rice straw depended less on rice variety (varies not more than 1.17 times) than on its content of extractive substances (varies 2.4 times).
2. The rice variety mostly affected the characteristics of the amorphous silica. Its specific surface was 8.6 to 102.4 m^2/g, and the average pore diameter was 6.9 to 85.7 nm. The sorption capacity relative to the organic dyes (methylene blue and brilliant green) varied by as much as a factor of two.

3. Such peculiarities of the different varieties of rice straw and the silica prepared from it needs to be taken into consideration in its use for production of silica-based materials with desirable properties, in particular, sorbents.

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