



## Processing Methods of Alkaline Hydrolysate from Rice Husk

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**Abstract:** This paper devoted to finding processing methods of alkaline hydrolysate produced from rice husk pre-extraction, and discusses alkaline hydrolysate processing scheme and disengagement of some products: amorphous silica of various quality, alkaline lignin, and water and alkaline extraction polysaccharides. Silica samples were characterized: crude (air-dried), burnt (no preliminary water treatment), washed in distilled water, and washed in distilled water and burnt. Waste water parameters upon the extraction of solids from alkaline hydrolysate dropped a few dozens or thousand times depending on the applied processing method. Color decreased a few thousand times, turbidity was virtually eliminated, chemical oxygen demand about 20–136 times; polyphenols content might decrease 50% or be virtually eliminated. The most prospective scheme obtained the two following solid products from rice husk alkaline hydrolysate: amorphous silica and alkaline extraction polysaccharide. Chemical oxygen demand of the remaining waste water decreased about 140 times compared to the silica-free solution.

**Key words:** rice; husk; alkaline hydrolysate; silica; lignin; polysaccharide

Fundamental and applied chemical and technological researches of naturally occurring plant-based compounds are currently aimed at deep processing of renewable plant resources to obtain a whole range of commercial products. Deep processing ensures a great reduction of dangerous waste and improves the ecological situation. The main consumer of plant materials traditionally is pulp and paper industry, using various kinds of wood. Recent years, a lot of literatures suggest the use of non-wood fibrous plant materials in the production process, including huge wastes of agricultural annual plants like lint, gumbo, hemp, rice, and oats.

Great renewable wastes left after rice production have long been a concern for many researchers all over the world as the source of fibrous materials and a number of chemicals. The main mineral component of rice production waste (husk and straw), as distinct from other grain crops, is amorphous silica. Rice production waste is a unique source of silica containing materials for various purposes (Cai et al, 2009; Pijarn et al, 2010; Zemnukhova and Fedorisheva, 2010; Issa et al, 2011; Zemnukhova et al, 2014). Besides silica, alkaline hydrolysate contains organic components such as lignin, polysaccharides, and low molecular tarry materials. Soda lignins are the true source of sulfur-free lignins,

which can be used in the production of composition materials, plastic and carbon fibers. Alkaline lignin is sedimented by pH regulation to establish acidic media (Deineko, 2012). Total polysaccharides yield from rice waste varies depending on the kind of plant and raw materials (husk or straw) from 8.2% to 26.1%. Water polysaccharides are mainly glucans. Polysaccharides upon alkaline extraction of rice husk contain debris of arabinose, xylose, glucose and galactose. Those polysaccharides show some inhibitor properties in connection with cancer cells and steel corrosion (Zemnukhova et al, 2004, 2006).

Comprehensive schemes for the production of valuable components from alkaline hydrolysate upon soda pulping of rice waste are a great concern. For example, Minu et al (2012) offer two-stage method for production of lignin and silica from black liquor in the lignocellulosic production of ethanol from rice husk. The scheme ensures good production quality and environmentally safe discharge by chemical oxygen demand (COD) and electric conductivity. Zhang et al (2013) showed a method aimed to obtain lignin-modified silica with 50–100 nm pore diameter using carbon dioxide.

Upon extraction of lignin from alkaline hydrolysate, lignin-containing waste water remains an issue which needs to

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be treated before discharge into water bodies. For the treatment, it is suggested to use photochemical oxidation (Chang et al, 2004), membrane filtering (Olsson, 2013), and electrocoagulation (Ugurlu et al, 2008; Zaied and Bellakhala, 2009; Lafi, 2011). Electrochemical oxidation of organic pollutants is a method for treatment from the substances resistant to biodegradation in future.

The anodic oxidation of some benzene derivatives (model organic pollutants) at platinum and dimensionally stable anodes was investigated (Comninellis, 1994). A number of studies showed that the electrochemical treatment is effective in treating the actual waste water of pulp and paper mill, such as black liquor from difficult-organic pollutants (Wang et al, 2008) and organic halides such as pentachlorophenol, which is formed during bamboo processing (Patel and Suresh, 2008). El-Ashtoukha et al (2009) used the electrochemical processing for waste water treatment at the paper mill, where the rice straw is used as a feedstock for the pulp production. The effectiveness of bleaching ranges from 53% to 100% depending on the operating conditions, and the average COD drops from 5 500 mg/L to 160 mg/L. For electrochemical oxidation of paper mill waste water, a reactor consisting of stainless steel rods electrodes can be used. Electrochemical treatment reduces the COD by 28% and the color by 93.7% (Perng et al, 2008). Electrochemical oxidation of paper mill waste water using anode composition, Ti/RuPb(40%)Ox, reduces the content of organic substances by 99%, and chromaticity and polyphenols by 95% (Zayas et al, 2011). It was shown that the use of electrochemical oxidation for the treatment of silicon-free waste water upon alkaline pre-extraction of rice husk ensures great reduction of hydrochemical parameters, enabling to assess the content of organic compounds (Zemnukhova et al, 2013). However, the literature analysis has shown that there is still no comprehensive scheme for deep processing of alkaline hydrolysate from rice husk including treatment of waste water.

The objectives of this study were to assess the possible ways for processing of alkaline hydrolysate produced from rice husk and to assess the quality of waste water upon the removal of solid products.

## MATERIALS AND METHODS

### Obtaining alkaline hydrolysate and silica containing compounds

The material of the research was rice husk, sampled in Krasnodar Krai, Russian Federation. Husk sample was sifted through sieve (2 mm particle size) to remove tiny fractions (bran siftings dust). Then, raw materials were washed in distilled water and air-dried and hydrolyzed by 1 mol/L sodium hydroxide when heated to 90 °C for 1 h in a laboratory reactor. Volumetric ration solid to liquid was 1 : 13. The hydrolysate developed was filtered through synthetic fabric with pore size of 15 µm, and alkaline hydrolysate (S1) was obtained.

Silica containing substances in form of silicic acid were obtained from S1 with simultaneous neutralization of alkaline solution. With that purpose, S1 was mixed with concentrated

hydrochloric acid with pH 6.0. Silicic acid was filtered through filter paper with pore size of 2–3 µm, and silica-free solution (S2) was obtained.

From the silicic acid extracted, four samples of silicium dioxide were obtained: No. 1, Crude (air-dried); No. 2, Burnt at 650 °C for 3 h (without preliminary washing with water); No. 3, Washed in distilled water; and No. 4, Washed in distilled water and burnt at 650 °C for 3 h.

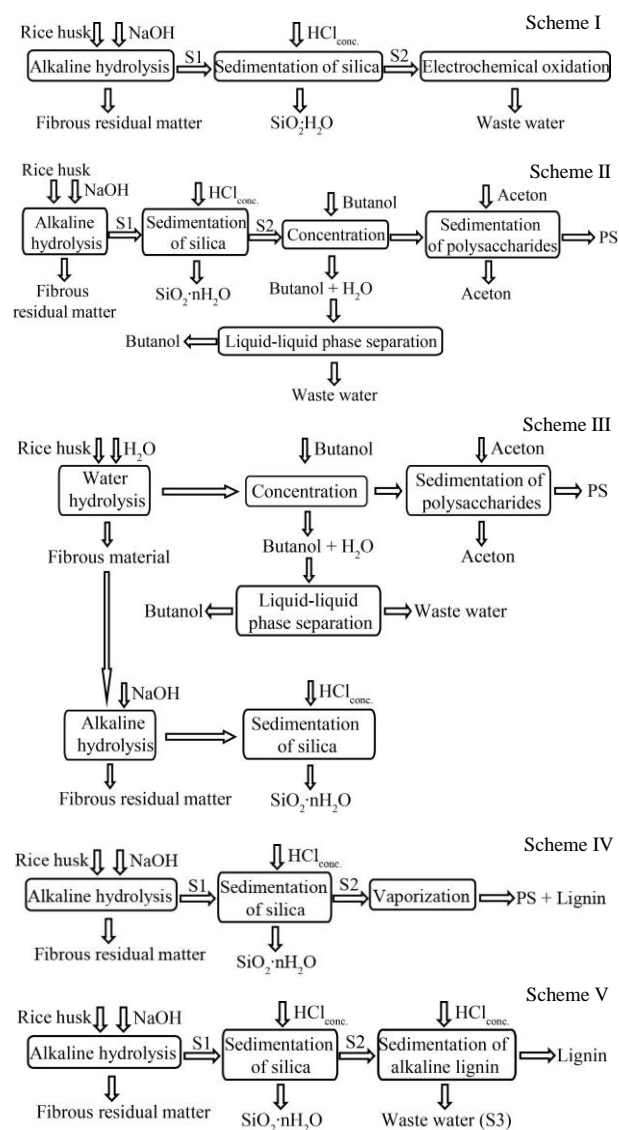
### Schemes for comprehensive processing of alkaline hydrolysate

Waste water discharged upon the extraction of silicic acid from S2 was processed according to schemes I–V (Fig. 1). Under the scheme I, S2 was electrochemically treated. Electrochemical oxidation of S2 was made in membraneless temperature-controlled electrolytic cell with constant stirring at anode current density 100 mA/cm<sup>2</sup> during 90 min. As an anode, laboratory's oxide ruthenic-titanium anode consists of 30% RuO<sub>2</sub> and 70% TiO<sub>2</sub>. As a cathode, Ti of BT1-0 grade was used. Electrochemical oxidation was made to silica-free solution of S2, diluted with distilled water for 10 times. According to the schemes II–V from S2 solution, solid products were obtained using various techniques. According to the scheme II, silica-free solution was concentrated by vaporization with butanol in rotary evaporator Hel-VAP Advantage HB/G38ML (Heidolph, Germany) at S2 : butanol ration equal to 3 : 1. For sedimentation of alkaline extraction polysaccharides (PS), acetone was added into concentrated solution with 1 : 4 by volume. The residual polysaccharides matter was separated by centrifuging and air-dried. Scheme III was different from other schemes by the existence of water hydrolysis of raw materials for 3 h prior to alkaline hydrolysis. The filtrate upon water hydrolysis was concentrated with butanol in a rotary evaporator and then water extraction polysaccharides were sedimented. Rice husk was undergoing alkaline hydrolysis upon water hydrolysis with further production of silica. The silica-free solution was evaporated, followed by production of lignin-polysaccharide residual matter which was air-dried. According to the scheme IV, silica-free solution was evaporated, lignin-polysaccharide residual matter was produced and then air-dried. According to the scheme V, from silica-free solution produced upon the removal of silica-containing compounds, alkaline lignin was sedimented by acidification with hydrochloric acid to pH 2.0. The sedimented alkaline lignin was filtered through filter paper with pore size 2–3 µm, washed with water at pH 2.0 and air-dried (Lora and Glasser, 2002).

### Determination of waste water quality parameters

Color and turbidity were determined by the photoelectrocolorimetric method on spectrophotometer UNICO-1201 (United Products & Instruments Inc., USA). COD was determined by photometric method, and pH was measured by a pH-meter with glass electrode. Phenol equivalent content was determined by photometry, using Folin's reaction with Folin's phenol agent (Clescerl, 1998).

Determination of biochemical oxygen demand (BOD<sub>5</sub>) was performed according to the protocol (Directive document



**Fig. 1. Schemes of comprehensive processing of alkaline hydrolysate.**

Scheme I, Processing with further electrochemical treatments of waste water; Scheme II, Processing with alkaline extraction of polysaccharides (PS); Scheme III, Processing with water extraction of polysaccharides and lignin polysaccharides residue; Scheme IV, Processing with lignin polysaccharides residue by vaporization; Scheme V, Processing with alkaline lignin preparation.

S1, Alkaline hydrolysate; S2, Silica-free solution.

52.24.420-2005, 2005). The determination was based on the measurement of the mass concentration of dissolved oxygen by the titrimetric iodometric method in a water sample before and after 5 d incubation under the standard conditions (20 °C, absence of air and light). The sample was placed into a flask with volume of 2 dm<sup>3</sup>, and then adjusted to a temperature of (20 ± 1) °C by heating (using a water bath) or cooling (under running water). Then, the sample was vigorously shaken at least 10 min to saturate it with oxygen. After completing the saturation procedure, the sample was left for 3–5 min to

remove excess air. The prepared sample was poured into three dry oxygen bottles. In one of them, we immediately measured concentration of dissolved oxygen by the Winkler method. The other two were capped and incubated without light in an incubator at (20 ± 1) °C for 5 d. After this period, we determined the concentration of unencumbered dissolved oxygen in the incubated flasks. BOD test was carried out by dilution. Dilution water was prepared on the application day from distilled water at 20 °C with addition of phosphate buffer solution, solutions of magnesium sulfate, calcium chloride and iron chloride at the rate of 1 cm<sup>3</sup>/dm<sup>3</sup>. Then, water was saturated with oxygen in the air by vigorous shaking and then left for 3–5 min to establish equilibrium. BOD<sub>5</sub> was also determined in the dilution water. For this purpose, four oxygen flasks were simultaneously filled with water for diluting samples. In two of them, we immediately determined the concentration of dissolved oxygen, and the other two were placed into the incubator together with the party of the analyzed samples and determined the dissolved oxygen concentration after incubation.

### Instrumental methods

X-ray phase analysis of silica samples was made in Cu K<sub>α</sub>-rays on the diffractometer Bruker D8 Advance (Germany). Specific surface (*S<sub>sp</sub>*) was determined by the Brunauer-Emmett-Teller (BET) method on the analyzer ASAP 2020 (Micromeritics Instrument Corporation) by nitrogen adsorption.

## RESULTS AND DISCUSSION

In all the schemes I–V (Fig. 1), at the first stage, two valuable products were obtained (fibrous residual matter which is the raw material for further pulping, and amorphous silica). Dry fibrous matter yield was about 63% of the initial mass of raw materials, and upon treatment from alkali about 54% (Fig. 1). According to the scheme III, dry treated fibrous matter yield upon water hydrolysis was about 90%, and upon alkaline hydrolysis about 45%. Crude silica yield was about 50%, burnt about 29%, washed and air-dried about 19%, and washed and burnt about 9%.

In the scheme I, waste water was electrochemically treated upon silica separation. In the scheme II, waste water appeared upon the concentration of silica-free solution of S2 by butanol. The yield of air-dried PS by alkaline extraction (crude) was 7%–8%. In the scheme III, the yield of crude PS of water extraction was about 1%, and lignin polysaccharides residual matter about 20%. Waste water appeared at the stage of water hydrolysate concentration upon its separation from butanol. In the simplest scheme IV, for the processing of rice husk, only silicium dioxide and lignin polysaccharides residue were obtained, and the yield was about 24%. Upon vaporization, no waste water was left. In the scheme V, the yield of alkaline lignin was about 0.5%. Waste water appeared upon the removal of alkaline lignin from the solution of S2. Table 1 lists the

quality parameters of waste water as per the schemes I–V.

Upon the removal of silica-containing compounds from S1, all quality parameters were improved by a few times: color by 7 times, turbidity by 4 times, COD by 3 times, BOD<sub>5</sub> by 6 times, and phenolic compounds by 2 times. Comparison of S2, other waste waters obtained when applying various processing methods showed that all parameters were decreasing a few dozens and thousands of times depending on the method for the processing. pH of solution from alkaline media changed into acidic media or close to neutral, color decreased a few thousand times, up to colorless solution, turbidity was virtually disappearing, COD dropped by 20–136 times, BOD<sub>5</sub> also tended for decrease, phenolic compounds content may drop by 50% or almost disappear in waste water (scheme I).

Table 2 shows indicators of waste water quality before and after the electrochemical treatment of alkaline hydrolysates obtained in this study compared with the published data (Mahesh et al, 2006; El-Ashtoukhy et al, 2009). It also shows the conditions of the electrochemical oxidation process.

It should be noted that a comparative analysis is difficult to perform, because, firstly, in these studies (Mahesh et al, 2006; El-Ashtoukhy et al, 2009), they use mixing scheme of Palp and Paper Industry waste water into a single stream, which is formed at the stages of obtaining and refining (bleaching) pulp, and black liquors entering the electrochemical treatment differ significantly compared with the results of this study, and secondly, they use different methods of cooking plant raw materials and different conditions of the electrochemical

treatment. A significant reduction in the color achieved in the present study can be noted. COD results were worse by 2–4 times due to a higher content of organic compounds in the monitored waste water.

In Table 1, COD in waste water upon separation of butanol in schemes with PS extraction (schemes II and III) decreased by 132–136 times. In those schemes, PS was established and may be useful as biologically active substance, the properties of which are a little described in literature (Zemnukhova et al, 2004), or corrosion inhibitors (Zemnukhova et al, 2006). The most interesting scheme is scheme II, as the yield of PS was higher (7%–8%), and it consisted of a smaller number of technological stages.

Scheme IV may be prospective as there was no discharged water. However, the properties determining the field of use of the solid product developed under that scheme—lignin polysaccharides residue have not been studied yet.

Waste water appearing in scheme V is different from other waste water by low pH, at which alkaline lignin is sedimented. Upon the removal of alkaline lignin in the solution, quality parameters of waste water decreased by 1.5–5.0 times. According to the given scheme, we obtained the alkaline lignin with the yield of 0.5%, and the composition, which is constant for this kind of raw materials, is different from hydrolysis lignin established in the pulping of wood. Table 3 lists the description of silica-containing substances obtained from S1.

Color, yield and  $S_{sp}$  of silica depended on the preparation conditions of the final product (Table 3). For example,  $S_{sp}$  may

**Table 1. Quality parameters of waste water upon processing of rice husk alkaline hydrolysate by various schemes.**

Solution processing scheme	pH	Color	Turbidity (mg/L)	COD (mg/L)	BOD <sub>5</sub> (mg/L)	Polyphenol (mg/L)
S1	13.9	95 000	3 205	50 804	34 317	1 833
S2	5.9	13 833	769	17 096	5 673	1 094
Scheme I	5.8	10	7	847	71	< 0.025
Scheme II	6.6	2	2	126	—	—
Scheme III	4.6	5	1	130	—	—
Scheme V (S3)	2.4	2 346	132	12 800	6 421	750

COD, Chemical oxygen demand; BOD<sub>5</sub>, Biochemical oxygen demand; S1, Alkali hydrolysate; S2, Silica-free solution.

‘—’ means the parameter was not determined. There was no waste water for scheme IV.

**Table 2. Comparative analysis of electrochemical treatment of alkaline hydrolysate obtained from non-wood plant raw material.**

Waste water quality indicator	Alkaline hydrolysate of rice husk (In this work)		Black liquor of wheat straw (Sulphate pulping) <sup>a</sup>		Black liquor of rice straw (Sodium hydroxide pulping) <sup>b</sup>	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
Color (Degree)	13 833	10	1 750	175	Brown	—
BOD <sub>5</sub> (mgO <sub>2</sub> /L)	5 673	—	615–670	50	300–400	—
COD (mgO/L)	17 096	847	2 000–2 100	410	5 000–6 000	160
Conditions of electrochemical treatment						
Material of the electrodes (cathode and anode)	Anode: Ruthenium oxide-titanium; Cathode: Commercial titanium (Brand BT1-0)		Anode-Cathode: Iron (Magnetite Fe <sub>3</sub> O <sub>4</sub> )		Anode: lead sheets (PbO <sub>2</sub> ); Cathode: stainless steel	
Current density (mA/cm <sup>2</sup> )	100		5, 6		6, 6	
Electrolysis time (min)	90		90		60	
Volume of the cell (mL)	50		2 000		—	
NaCl concentration (g/L)	4 <sup>c</sup>		0.625 <sup>d</sup>		1 <sup>b</sup>	

BOD<sub>5</sub>, Biochemical oxygen demand; COD, Chemical oxygen demand.

‘—’ means the parameter was not determined. <sup>a</sup>, Data from Mahesh et al (2006); <sup>b</sup>, Data from El-Ashtoukhy et al (2009); <sup>c</sup>, NaCl concentration in diluted solution ( $n = 1 : 10$ ); <sup>d</sup>, Concentration of the supporting electrolyte NaCl.

**Table 3. Description of silicium dioxide samples obtained from rice husk alkaline hydrolysate.**

Sample	Product	Color	Yield (%)	SiO <sub>2</sub> (%)	S <sub>sp</sub> (m <sup>2</sup> /g)	x-ray phase analysis
No. 1	Crude	Brown	50	36	5.9	AP + NaCl
No. 2	Burnt at 650 °C	Black	29	60	5.6	AP + NaCl + Cristobalite
No. 3	Washed and air-dried	Beige	19	96	59.2	AP
No. 4	Washed and burnt at 650 °C	White	9	99	35.8	AP

AP, Amorphous phase; S<sub>sp</sub>, Specific surface.

be varied from 5.9 to 479.0 m<sup>2</sup>/g as in Zemnukhova et al (2014). As shown in Fig. 2, all samples are in amorphous phase, and in sample No. 2, there is crystal phase in the form of  $\alpha$ -cristobalite (Fig. 2-B). There is halite in samples No. 1 and No. 2 as impurity (Fig. 2-A and -B).

The analysis of schemes for comprehensive processing of alkaline hydrolysate shows that it is possible to obtain a fibrous residual matter, precipitated silica of a various quality, polysaccharides, lignin-polysaccharide residual matter and alkaline lignin. From the above mentioned products, we most fully studied the properties of the fibrous residual matter, precipitated silica and polysaccharides. The fibrous residual matter can be used to produce chlorine-free bleached pulp by chlorine-free method (Vurasko et al, 2007). The precipitated silica of different qualities can be used as a sorbent (Arefieva et al, 2015; Kholomeidik et al, 2015).

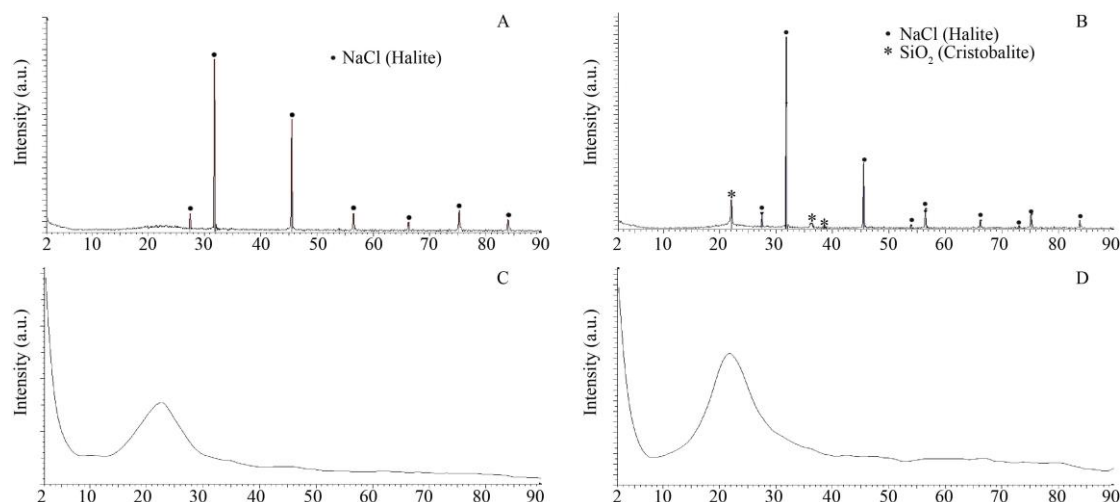
Polysaccharides of water oxalate and alkaline extraction isolated from rice waste was studied previously (Zemnukhova et al, 2004). The following information was obtained: (1) We obtained the content of PS in husk, straw and rice husking bran. Total yield of PS from rice waste varies depending on the type of plant and raw materials (husk, straw or husking bran) in the range of 8.2%–26.1%; (2) We studied PS chemical composition. It was shown that PS from rice waste (particularly water and oxalate) mainly contained glucans (22% in alkaline extracts, up to 100% in water and oxalate ones); rhamnose and mannose are virtually absent; arabinose, xylose and galactose are present in minor amounts. Most arabinose (19%–20%) and xylose (26%–46%)

are in the alkaline extracts. Uronic acids are found only in trace amounts in some extracts of rice husk. We also found traces of inositol; (3) x-ray diffraction analysis and IR spectroscopy help to obtain some information about the structure of the substances. It was shown that PS has amorphous, crystalline or amorphous-crystalline state. The analysis of the infrared spectra in the 400–4 000 cm<sup>-1</sup> shows the ability to quickly monitor the quality of the product; (4) We held an evaluation of cytotoxic activity of several PS samples obtained from rice husks on human tumor cells K562. It was found that polysaccharides isolated from oxalate and alkaline extracts of rice husk have the most cytotoxic activity (Mamontova et al, 2005).

Of course, the question of the rice waste PS use in practice requires additional research, which is beyond the scope of this work. The alkaline lignin and lignin-polysaccharide residual matter are studied not that well. Currently the properties of alkali lignin as compared to hydrolytic lignin and Klasson lignin from rice husk are under study (Gnedenkov et al, 2015). A further study is required for industrial purposes.

## CONCLUSIONS

The processing methods of alkaline hydrolysate produced from rice husk pre-extraction have been studied for further obtaining the following solid products: amorphous silicium dioxide of various quality, alkaline lignin, water and alkaline extraction polysaccharides. It was found that quality parameters of waste

**Fig. 2. x-ray diffraction patterns of silica dioxide.**

A, Crude (No. 1); B, Burnt (No. 2); C, Washed and air-dried (No. 3); D, Washed and burnt at 650 °C (No. 4).

water are improved to various degrees upon the removal of solid products depending on the processing method. From the alkaline hydrolysate processing schemes suggested, alkali extraction of polysaccharides is the most prospective. According to that scheme, two valuable products were obtained: amorphous silica dioxide and alkaline extraction polysaccharides, meantime the integral COD of the remaining waste water compared to the silica-free solution is decreasing by about 140 times.

## REFERENCES

- Arefieva O D, Zemnukhova L A, Morgun N P, Rybin V G, Tsvetnov M A, Kovshun A A, Panasenko A E. 2015. Removal of (2,4-dichlorophenoxy) acetic acid from aqueous solutions using low-cost sorbents. *Air Soil Water Res*, **8**: 59–65.
- Cai X, Hong R Y, Wang L S, Wang X Y, Li H Z, Zheng Y, Wei D G. 2009. Synthesis of silica powders by pressured carbonation. *Chem Eng J*, **151**: 380–386.
- Chang C N, Ma Y S, Fang G C, Chao A C, Tsai M C, Sung H F. 2004. Decolorizing of lignin wastewater using the photochemical UV/TiO<sub>2</sub> process. *Chemosphere*, **56**(10): 1011–1017.
- Clescerl L S. 1998. Standard Methods for the Examination of Water and Wastewater. 20th Edition. Washington, USA: American Public Health Association: 988–992.
- Comninellis C. 1994. Electrochemical oxidation of organic pollutants for wastewater treatment. *Stud Envi Sci*, **59**: 77–102.
- Deineko I P. 2012. Disposal of lignins: Achievements, problems and prospects. *Chem Plant Mater*, **1**: 5–20.
- Directive document 52.24.420-2005. Biochemical Oxygen Demand in the Waters: Methodology for Defining by Bottle Method. the Russia Federation.
- El-Ashtouky E S Z, Amin N K, Abdelwaha O. 2009. Treatment of paper mill effluents in a batch-stirred electrochemical tank reactor. *Chem Eng J*, **146**(2): 205–210.
- Gnednikov S V, Opra D P, Zemnukhova L A, Sinebrukhov S L, Minaev A N, Kedrinskiy I A, Sergienko V I. 2015. Electrochemical performance of Klason lignin as the positive electrode material for lithium-current source. *Chem Plant Mater*, **2**: 239–248.
- Issa R M, Abou-Sekkina M M, Bastawisy A M, Khedr A M, El-Helece W A. 2011. New treatment of the black liquor produced from pulping of rice straw. *Elixir Chem Phys*, **33**: 2276–2278.
- Kholomeidik A N, Nikolenko Y M, Zemnukhova L A, Ustinov A Y, Mayorov V Y, Polyakova N V. 2015. Study of rice husk silica adsorption with the respect to copper ions(II) and manganese(II). *Chem Plant Mater*, **3**: 169–176.
- Lafi W K. 2011. Electro-coagulation treatment of wastewater from paper industry. In: Recent Researches in Energy, Environment, Devices, Systems, Communications and Computers. International Conference on Energy, Environment, Devices, Systems, Communications, Computers. Venice, Italy: 61–69.
- Lora J H, Glasser W G. 2002. Resent industrial application of lignin: A sustainable alternative to nonrenewable materials. *J Polym Environ*, **10**(1/2): 39–48.
- Mahesh S, Prasad B, Mall I D, Mishra I M. 2006. Electrochemical degradation of pulp and paper mill wastewater: Part 1. COD and color removal. *Ind Eng Chem Res*, **45**(8): 2830–2839.
- Mamontova V A, Tomshich S V, Komandrova N A, Zemnukhova L A. 2005. Polysaccharides from rice production waste. In: Proceedings of the III International Conference. Minsk, the Republic of Belarus.
- Minu K, Jiby K K, Kishore V V N. 2012. Isolation and purification of lignin and silica from the black liquor generated during the production of bioethanol from rice straw. *Biomass Bioenerg*, **39**: 210–217.
- Olsson J. 2013. Separation of lignin and hemicelluloses from black liquor and pre-treated black liquor by nanofiltration. *Dep Chem Eng*, **2**: 1–6.
- Patel U D, Suresh S. 2008. Electrochemical treatment of pentachlorophenol in water and pulp bleaching effluent. *Sep Pur Technol*, **61**(2): 115–122.
- Perng Y S, Wang I C, Yu S T, Lin Y F. 2008. Application of an electro-oxidation treatment method to industrial paper mill effluents in the lab. *Taiwan J Forest Sci*, **23**(2): 111–123.
- Pijarn N, Jaroenworarluck A, Sunsaneeyametha W, Stevens R. 2010. Synthesis and characterization of nanosized-silica gels formed under controlled conditions. *Powder Technol*, **203**(3): 462–468.
- Ugurlu M, Gurses A, Dogar C, YalcIn M. 2008. The removal of lignin and phenol from paper mill effluents by electrocoagulation. *J Environ Manag*, **87**(3): 420–428.
- Vurasko A V, Driker B N, Zemnukhova L A, Galimova A R. 2007. Resource-saving technology for producing pulp at complex processing of rice straw. *Chem Plant Mater*, **2**: 21–25.
- Wang B, Chang X, Ma H Z. 2008. Electrochemical oxidation of refractory organics in the coking wastewater and chemical oxygen demand (COD) removal under extremely mild conditions. *Ind Engin Chem Res*, **47**(21): 8478–8483.
- Zaieda M, Bellakhal N. 2009. Electrocoagulation treatment of black liquor from paper industry. *J Hazard Mater*, **163**: 995–1000.
- Zayas T, Picazo M, Salgado L. 2011. Removal of organic matter from paper mill effluent by electrochemical oxidation. *J Water Res Prot*, **3**(1): 32–40.
- Zemnukhova L A, Arefieva O D, Kovshun A A. 2013. Treatment of alkaline waste water generated by the hydrolysis of rice husk. *Adv Mater Res*, **781/784**: 2087–2090.
- Zemnukhova L A, Tomshich S V, Mamontova V A, Komandrova N A, Fedorisheva G A, Sergiyenko V I. 2004. Study of structure and properties of rice husk polysaccharides. *J Appl Chem*, **77**(11): 1901–1904.
- Zemnukhova L A, Chernov B B, Schetinina G P, Kharchenko U V, Fedorisheva G A. 2006. Method for Steel Protection From Corrosion. The Russian Federation, Patent 2289639.
- Zemnukhova L A, Fedorisheva G A. 2010. Method for Obtaining Silica Dioxide. The Russian Federation, Patent 2394764.
- Zemnukhova L A, Panasenko A E, Tsoi E A, Fedorisheva G A, Shapkin N P, Artemyanov A P, Maiorov V Y. 2014. Composition and structure of amorphous silica produced from rice husk and straw. *Inorg Mater*, **50**(1): 75–81.
- Zhang X J, Zhao Z H, Ran G J, Liu Y, Liu S, Zhou B, Wang Z. 2013. Synthesis of lignin-modified silica nanoparticles from black liquor of rice straw pulping. *Powder Technol*, **246**: 664–668.

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