Available online at www.sciencedirect.com

ScienceDirect

Rice Science, 2017, 24(4): 235−240

Processing Methods of Alkaline Hydrolysate from Rice Husk

Olga D. AREFIEVA[1], Liudmila A. ZEMNUKHOVA[1,2], Anastasia A. KOVSHUN[1], Anna V. KOVEKHOVA[1]

([1]*Far Eastern Federal University, Vladivostok 690950, Russian Federation;* [2]*Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, Vladivostok 690022, Russian Federation*)

Abstract: This paper devoted to finding processing methods of alkaline hydrolysate produced from rice husk pre-extraction, and discusses alkaline hydrolysate processing schemed 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 demanded 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; Pijiarn et al, 2010; Zemnukhova and Fedorischeva, 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

Received: 20 August 2016; **Accepted:** 21 April 2017

Corresponding author: Olga D. AREFIEVA (arefeva.od@dvfu.ru)

Peer review under responsibility of China National Rice Research Institute

http://dx.doi.org/10.1016/j.rsci.2017.04.003

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-Ashtoukhya 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 ºC 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 ºC 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 ºC 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^2 during 90 min. As an anode, laboratory's oxide ruthenic-titanium anode consists of 30% RuO_2 and 70% TiO_2. 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_5) was performed according to the protocol (Directive document