UDC 542.06:628.386:633.258

Composition and Purification of Wastewater from the Alkaline Hydrolysis of Rice Shuck

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(Received March 18, 2011)

Abstract

Alkaline hydrolyzates obtained from rice shuck processing were investigated. Results of the purification of alkaline hydrolyzates by means of coagulation, neutralization with the release of silicic acid, and sorption are presented. It is demonstrated that the purification methods used do not provide the requirements for preliminarily purified and fresh water for use in manufacturing unbleached cellulose with respect to the main hydrochemical parameters (coloration, mineralization, pH). It is established that alkaline hydrolyzates can be utilized with the formation of amorphous silicon dioxide which has a broad range of applications.

Key words: rice shuck, alkaline hydrolysis, purification methods, silicon dioxide

INTRODUCTION

Traditionally, major amounts of water used in the course the pulp and paper production from wooden raw is returned into water reservoirs in the form of waste water. The latter represent a complex polydisperse system characterized by a high content of suspended solid substance (fibre and kaolin), changing pH value, a substantial chromatic level and a high biochemical oxygen demand (BOD) value [1]. Known waste water treatment methods for using in circulating water supply schemes in the pulp-and-paper industry involve the stages of filtration, treatment by reagents, decolorizing [2, 3]. In recent years, wide application was possessed by physicochemical wastewater treatment methods such as catalytic [4] and photocatalytic oxidation [5–7]; sorption with the use of diatomaceous earth and activated carbon [8], coagulation using various mineral coagulants (aluminum sulphate (alumina) $Al_2(SO_4)_3 \cdot 18H_2O$, sodium aluminate $NaAlO_2$, aluminum oxychloride $Al_2(OH)_5Cl$, sludge wastes and spent solutions from several manufactures) [9, 10]. Adsorbents for an adsorption-coagulation-biological treatment were proposed [11]. Choosing a method of wastewater treatment depends on several factors, including the method of treatment and chemical composition of the feedstock under consideration.

The source of cellulose could be presented also by non-wood raw materials, in particular crop wastes of annual plants. The main advantage of this raw material consists in its annual repeatability, low cost and almost constant chemical composition for the same plant species. The authors of [12] proposed a method for producing bleached cellulose using chlorine-free rice shuck and straw with preliminary feedstock treatment with sodium hydroxide and subsequent washing with water to obtain neutral pH of cleansing waters. At the same time, the authors of this work did not propose a scheme of wastewater treatment, whose composition in the case of using annual plants as a raw material is almost not available from the literature.

This paper is devoted to studying alkaline hydrolyzate, cleansing and waste waters formed in the course of producing cellulose from rice shuck, and searching for the methods of water treatment according to the main hydrochemical parameters (BOD_5, salinity, pH, and colour).

EXPERIMENTAL

All the experiments were performed with rice shuck (RSh-2 Catalogue IC, FEB RAS [13], [14]), taken in the Krasnodar Region. A sample of shuck was sieved through a sieve (particle size of 2 mm) for removal of fine fractions (bran, dust), then it was washed with distilled water and air-dried.

The hydrolysis of the raw material was performed using 1 M NaOH solution by means of heating up to 90 °C for 1 h. The solid-to-liquid volume ratio S/L amounted to 1 : 13. The resultant hydrolyzate was filtered to obtain solution No. 1 (S1). The filter cake (technical cellulose) was washed with water at a volume ratio S/L = 1 : 12. The process of washing the precipitate was continued until a neutral pH value of cleansing water (CW). Then CW was collected in one container to purify on a two-layered filter consisting of the layers of quartz sand and rice shuck ash resulted from combustion in the boiler room, Jilin (China). Rice shuck ash has dark colour and contains up to 86–90 % of silicon dioxide representing a mixture of amorphous and crystalline forms. The filtering materials were placed in a column of 50 mm in diameter. The height of the lower layer (rice shuck ash) was equal to 40 mm, the upper layer of sand being of 40 mm high, too. The CW moved downward with a flow rate of 56 mL/min. The filtrate was sampled into a cone flask; the first filtrate portions (50 mL) were discarded. In total, 2500 mL of filtered water (FW) was sampled.

For the purification of the alkali hydrolyzate (S1) we used a coagulation treatment and reagent neutralization treatment with silicic acid extraction.

The coagulation treatment was performed using aluminum sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ either without preliminary chlorination, or with preliminary chlorination in order to improve the course of coagulation and discoloration. The doses of a coagulant and that of chlorinated water were calculated in accordance with the Russian sanitary standard SNIP 2.04.02–84 [15]. After the coagulation treatment without preliminary chlorination and with preliminary chlorination we obtained solutions Nos. 2 (S2) and 3 (S3), respectively.

The reagent neutralization of the alkali hydrolyzate was performed using concentrated hydrochloric acid to obtain pH 6. The silicic acid formed in the course of neutralization was filtered to obtain solution No. 4 (S4). After passing the solution No. 4 through a bulk sorption filter consisting of sand and naturally occurring perlite layers (the Nachikinskoye deposit of the Kamchatka Region), we obtained solution No. 5 (S5).

According to the chemical composition, perlite consists of SiO_2 (68.2 %) and Al_2O_3 (16.83 %) mixture. In this work we used perlite fraction with the particle size of 1–2 mm, the total porosity of the sorbent being equal to 13 %, the micropore volume being of 0.001 cm^3/g. This sorbent was characterized in [16].

For the hydrolyzate (S1), CW, FW and solutions S2–S5 we determined the following quality parameters of wastewater: coloration [17], dry solid residue content and mineralization level (salinity) [18], pH, biochemical oxygen demand (BOD_5) [19]. The hydrochemical parameters such as salinity pH and coloration are under monitoring in the fresh water in the course of producing unbleached cellulose [20], whereas the parameter of BOD_5 was additionally chosen for further characterizing the content of microbiologically oxidized substances.

The concentration of a number of elements in the hydrolyzate was determined by means of atomic absorption spectroscopy (AAS) using an AA-770 spectrophotometer (Nippon Jarrell Ash, Japan) in the acetylene-air flame.

The X-ray diffraction analysis of silica was carried out using CuK_α radiation, a Bruker D8 ADVANCE diffractometer (Germany), whereas the IR absorption spectra of the samples were registered within the range of 400–4000 cm^{-1} in liquid paraffin, by means of a Shimadzu FTIR Prestige-21 Fourier spectrometer (Japan).

RESULTS AND DISCUSSION

The composition of rice shuck RSh-2 contains organic and inorganic substances, whose content depends on the plant cultivar [13, 14]. The main inorganic component of rice shuck is presented by silica in the amorphous state. The ash content in RSh-2 amounted to 20.5 %. The ash exhibited the following composition (mass %): SiO_2 91.71, Na_2O 0.026, K_2O 2.23, MgO 0.61, CaO 0.59, ZnO 0.011, MnO 0.11, CuO 0.001, Al_2O_3 0.16, Fe_2O_3 0.14.

In the course of RSh-2 treatment in the solution of sodium hydroxide, water-soluble substances of different composition (organic and inorganic) are extracted. The colour of the solution grows dark brown due to the presence of plant phenolic compounds. Among organic substances of such solutions there are polysaccharides most extensively studied, whose yield with respect to RSh-2 mass amounts to 10.7 % [14]. The main element in the inorganic alkaline hydrolyzate is silicon extracted from the shuck as sodium silicate, whereas the desilicated residue of RSh-2 can serve as a raw for cellulosic material according to [12]. The content of water-soluble substances in the RSh-2 in the case when it is processed with sodium hydroxide is equal to 45.15 mass %. Table 1 presents data concerning the content of inorganic elements in the hydrolyzate (S1) and solution S4. It can be seen that the content of silicon, manganese, and aluminum in the S1 is higher than it is required by the standards for drinking water and cultural purpose water [21]. So, the concentration of silicon in the hydrolyzate is equal to 345 MPC, manganese – 3.2 MPC, aluminum – 5 MPC.

The main hydrochemical indicators for S1, CW and FV are presented in Table 2, wherein also the requirements for the pre-purified and fresh water used in the production of unbleached cellulose are displayed [20]. One can see that all the parameters of the hydrolyzate exceed to a great extent the regulatory requirements. For the CW collected the values are reduced, but they do not meet the required standards of water quality. The mineralization level, coloration and total organic content determined from the difference between dry solid residue and salinity exhibited an order of magnitude decrease. The content of microbiologically oxidized organic matter (BOD_5) demonstrated no significant decrease.

All the parameters for CW do not amount up to normal values, too. The values of pH, salinity, and the total content of organic substances in the filtered water exhibited no changes, the value of BOD_5 demonstrated a 3-fold decrease, whereas the coloration caused by the presence of predominantly organic substances showed a 6-fold decrease.

So, our studies demonstrated that the CW formed *via* washing the residue of rice shuck after alkaline hydrolysis by 1 M NaOH solution cannot be reused in the manufacturing of unbleached cellulose. In order to reduce the total discharge level of wastewater it is desirable to eliminate the washing stage from the flowchart of technical cellulose obtaining based on rice shuck.

Table 2 also presents data concerning the main hydrochemical parameters for alkaline hydrolyzate with no preliminary chlorination (S2) and with preliminary chlorination (S3). It is seen that after the coagulation treatment of alkaline hydrolyzates the values of hydrochemical parameters show a decrease, whereas they do not satisfy the requirements for fresh water in manufacturing unbleached cellulose. In the case of the coagulation process without preliminary chlorination the value of BOD_5 exhibited a three-fold decrease, whereas with the preliminary chlorination we observed a four-fold decrease of this value. The total content of organic substances determined from the difference between solid dry residue and min-

TABLE 1

Content of elements in the alkaline hydrolyzate of rice shuck before (S1) and after (S4) the precipitation of silicic acid, μg/mL

Solutions	Si	K	Ca	Mg	Zn	Mn	Cu	Al	Fe
P1	3449.0	292.0	5.35	0.53	0.32	0.32	0.10	1.00	0.22
P4	34.04	2.05	0.05	0.01	0.01	0.01	>0.01	0.01	0.01

TABLE 2

Quality parameters of alkali hydrolyzate (S1), cleansing water (CW), filtered water (FW), wastewater after the coagulation treatment without preliminary chlorination (S2) and with preliminary chlorination (S3), after silicic acid precipitation (S4) and sorption purification procedures (S5)

Parameters	S1	CW	FW	S2	S3	S4	S5	Requirements for fresh water in manufacturing unbleached cellulose [20]
BOD_5, mgO_2/L	34 317±7132	27 473±1247	8600±1314	10 559±1267	7584±1293	15 000±2483	9467±1250	
Mineralization level, mg/L	62 516±1109	2178±333	2200±430	34 833±717	52 300±430	61 567±788	49 700±430	500
Dry solid residue, mg/L	104 133±25227	3320±387	3133±287	67 333±573	84 400±860	77 833±717	61 700±430	
pH	13.41±0.70	10.27±0.37	9.64±0.28	13.21±0.50	12.81±0.47	8.91±0.25	8.45±0.23	6.5–8.0
Coloration level, degrees	180 000±21500	31 800±860	5167±717	75 167±717	75 667±1433	161 667±7167	12 167±717	100
Water consumption, mL (per 50 mg of raw material)			9600					

eralization level decreased by 20 % both with the preliminary chlorination, and without it. The discoloration of the treated hydrolyzates (according to the coloration level) amounted to 50 %. The content of microbiologically oxidized substances in solution S3 as compared to solution S2 decreased slightly (by 28 %). Consequently, the preliminary chlorination of alkaline hydrolyzate included in the coagulation water treatment technology for improving the course of coagulation and discoloration, exhibits no significant influence on the content of organic matter. To all appearance, the colloidal particles of organic compounds contained in alkaline hydrolyzates, are of hydrophobic or low hydrophilic nature.

The neutralization of the hydrolyzate, wherein the amorphous silica extracted from rice shuck exists in the form of soluble sodium orthosilicate Na_4SiO_4, results in the formation of silica precipitate according to the following reactions:

$Na_4SiO_4 + 4HCl \rightarrow 4NaCl + H_4SiO_4$

$H_4SiO_4 \rightarrow 2H_2O + SiO_2\downarrow$

The precipitated silica was separated from the mother liquor (S4), washed with water until a negative qualitative reaction with respect to Cl^-, and dried at 105 °C (for complete water removal at 600 °C). The results of the analysis demonstrated that the water content amounts to about 3 %, whereas the content of the base material (SiO_2) in the product after the removal of water is more than 99 %. Using the XRD method we revealed that the resulting silica is amorphous: the XRD pattern exhibits a broad peak within the region $2\theta = 18{-}26°$ inherent in the amorphous structure of the substance. The analysis of the IR spectrum (Fig. 1) indicates that the absorption bands, according to [21], correspond to the vibrations of siloxane bonds Si–O–Si in the amorphous silica: deformation (463 cm^{-1}), symmetric stretching (802 cm^{-1}) and asymmetric stretching (1096 cm^{-1}) vibrations. The presence of water in the compound, which is characterized by IR spectral absorption bands in the region of stretching (3194, 3416, 3624 cm^{-1}) and deformation (1632 cm^{-1}) vibration of OH groups, results in the formation of silanol bond Si–OH with the absorption band at 966 cm^{-1}. According to the characteristics, the amorphous silica precipitated from the hydrolyzate (S1) meets the requirements of the Rus-

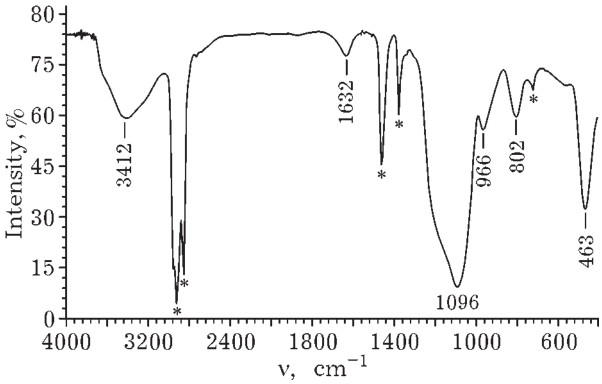

Fig. 1. Infrared absorption spectrum of amorphous silica. Symbol * denotes the absorption band of Vaseline oil.

sian State Standard GOST 4214–78 [22] and could be used, for example, in analytical chemistry, in pharmaceutics, perfumes, household chemicals, for the production of phosphors and rubber materials.

Table 2 demonstrates the quality parameters of alkaline wastewater after extracting the silicic acid (S4) therefrom, and further purifying the wastewater residue by means of the sorption on a filled double-layered sand and perlite filter (S5). It can be seen that all the quality parameters of waste water after the extraction of silicic acid and the subsequent sorption purification also do not meet regulatory requirements. In this case, S4 exhibited decreasing both BOD_5 and the total content of organic compounds. After the sorption purification by means of perlite, the value of BOD_5 demonstrated a 1.5-fold decrease, the total content of organic matter showed a 1.3-fold decrease, the coloration level decreased by an order of magnitude. As one can see from Table 1, the content of elements in the wastewater after the extraction of the silica decreased to a considerable extent. The concentration of aluminum and manganese reached the standards for drinking water and cultural and household purposes, the concentration of silicon decreased from 345 MPC to 3.4 MPC.

CONCLUSION

1. It was found that wastewaters (hydrolyzate) and cleansing waters formed in the course of alkaline hydrolysis of rice shuck does not satisfy the regulatory requirements for the prepurified and fresh water.

2. The treatment of cleansing water with a two-layer filtering load of rice shuck ash and sand is not efficient because a high content of pollutants.

3. The coagulation-based treatment of waste water (hydrolyzate) obtained via alkaline hydrolysis of rice shuck, results in solution discoloration and reduction of BOD_5 value. However, to achieve compliance with regulatory requirements for purified and fresh water used for manufacturing unbleached cellulose was of no success.

4. The wastewater (hydrolyzate) could be used as a source for extracting silicic acid which exhibits a wide range of applications. Waste water remaining after extracting silicic acid does not meet requirements for the discharge of waste water into natural water reservoirs or using them in a closed water recycling loop, so one needs to look for further ways to purify these wastewaters.

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