Influence of Rice Husk Processing Methods on the Chemical Composition of Bio-based Materials and Wastewater

David Castro 1, Olga Arefieva 1,2,* , Marina Vasilyeva 1,2, Anna Kovekhova 1,2

1 Far Eastern Federal University, Vladivostok, Russia
2 Russian Academy of Sciences, Institute of Chemistry, Vladivostok, Russia
* Correspondence: arefeva.od@dvfu.ru (O.A.);

Abstract: Bio-based materials from rice husk were obtained by processing rice rusk with acid (HCl, H2SO4, and H3PO4 0.1 mol·L-1), alkali (NaOH 0.1 mol·L-1, 0.25 mol·L-1 and 0.5 mol·L-1) and water. The chemical composition of rice husk, obtained from its bio-based materials and generated wastewater, was studied. After obtention of bio-based materials, wastewater produced in rice husk processing was treated by heterogeneous photo-Fenton. Substances soluble in water, pentosanes, lignin, cellulose, easy and difficult hydrolyzable polysaccharides were determined. Results showed that the chemical composition of rice husk and bio-based materials processed with water are similar. It is shown that bio-based materials processed with alkali contain more lignin, pentosans, and cellulose than when it is processed with water and acid. Wastewater, obtained while processing rice husk, was treated by a heterogeneous photo-Fenton process using SiO2-based RH-Fe-300 obtained from rice husk under visible and solar irradiation in the presence of hydrogen peroxide. Wastewater treatment by photo-Fenton presents decreased color, turbidity, phenolic compounds, and COD by 30-99% compared to the initial data. Achieved results are important for obtaining bio-based materials from rice husk and the treatment of wastewater generated during their production.

Keywords: rice husk; bio-based materials; chemical composition; photo-Fenton; treatment wastewater.

1. Introduction

Rice is a staple food for almost half of the world's population and is grown on the world's six continents (Asia, Africa, Australia, Europe, North America, South America) [1]. About 600 million tons of rice are produced annually worldwide. When processing rice, solid wastes are formed, 20% of which is rice husk, which gives an annual volume of rice husk - 120 million tons [2]. Rice husk consists mainly of cellulose (50%), lignin (25-30%), and silica (15-20%). Moisture content is usually 10-15%. The chemical composition of various rice husk samples varies depending on climatic conditions [2-4]. Cellulose is a polysaccharide consisting of several hundred to many thousands of β-bound D-glucose units. Lignin is a complex polymer of aromatic alcohols, known as monolignol, and it is an integral part of the secondary cell walls of plants and some algae. Lignin contains various functional groups: carbonyl, amide, amino, phenolic, carboxyl, hydroxyl, ester, and sulfhydryl groups that can complex. Usually,
lignocellulose biomass contains 56-72% of fermentable carbohydrates (cellulose and hemicellulose) by dry weight [5].

Rice husk can be used as a source of silicon for obtaining silica, aluminosilicates, and silicates [6, 7], cellulose fibers [8] as a potential energy resource [9] in ceramic and refractory industry, as a raw source for the production of xylitol, furfural, ethanol, acetic acid, lingo sulphonic acids, etc. [2]. Moreover, rice husk with or without processing is an excellent biosorbent to remove heavy metals and dyes from aqueous solutions [10]. Rice husk processing with acids or alkalis increases adsorption capacity and removes impurities and soluble organic compounds [11]. Diluted and concentrated acids like HCl, H2SO4, H3PO4, HNO3 as well as citric and tartaric acids are used for acid processing. Treatment with concentrated acids is executed in the case of agricultural wastes with great content of cellulose. Acid processing provides bio sorbents with irregular surfaces and a porous structure. In addition, processed rice husk has high sodium, silicon, and phosphorus content and less potassium and calcium than the original rice husks [12, 13]. FT-IR studies have shown new adsorption peaks as hydrogen-bonded OH and C=O stretch groups attributed to carboxylic acids, and the peak corresponds to C-O in the phenols [12–14]. For alkaline processing, NaOH, Ca(OH)2, NH3·H2O and Na2CO3 are mainly used. This method is favorable for biomass with fewer lignin components as agricultural wastes. This processing increases the number of galactonic acid groups formed during the hydrolysis of O-methyl ester groups, facilitating ion exchange with metal ions. Alkali processing results in delignification, incomplete hydrolysis of hemicelluloses, cellulose decrystallisation, and cellulose swelling. Also, this processing promotes the formation of a greater internal surface area, porous structure, and a lower degree of cellulose polymerization [13, 15, 16]. Rice husks and straws can also be changed by hydrothermal carbonation. Most studies on biosorption show that alkaline processing promotes the sorption of cations, while acidic processing is more effective for anions [13]. Different conditions for the processing of rice husk are given in Table 1. Particle size, dosage, solution, contact time, and temperature parameters are the most important for obtaining biosorbents. In most of the studies, the particle size was less than 1 mm for alkali processing diluted sodium hydroxide (0.1 mol·L⁻¹), and for acid processing, diluted acids are more used; dosage of bio-based materials depends on processing, contact time (usually 1 or 24 hours) and temperature (25°C) [15, 17-25].

<table>
<thead>
<tr>
<th>Type of processing</th>
<th>Condition</th>
<th>Particle size</th>
<th>Dosage</th>
<th>Solution</th>
<th>Contact time</th>
<th>Temperature</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>0.4 mm</td>
<td>5 g/60 mL</td>
<td>Citric acid 0.5 mol·L⁻¹</td>
<td>1 h</td>
<td>25°C</td>
<td>[17]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>1 g/2 mL</td>
<td>HCl 0.1 mol·L⁻¹</td>
<td>20 min</td>
<td>110°C</td>
<td>[18]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt; 1 mm</td>
<td>1 g/7 mL</td>
<td>Citric, salicylic, tartaric, oxalic, mandelic, malic, and nitrotriacetic acid 1.2 mol·L⁻¹</td>
<td>-</td>
<td>25°C</td>
<td>[19]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt; 1.19 mm</td>
<td>1 g/5 mL</td>
<td>H2SO4 13 mol·L⁻¹</td>
<td>20 min</td>
<td>175-180°C</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt; 1 mm</td>
<td>1 g/20 mL</td>
<td>HCl, H2SO4 and H3PO4 0.1 mol·L⁻¹</td>
<td>1 h</td>
<td>90°C</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Alkali</td>
<td>~2 mm</td>
<td>-</td>
<td>NaOH 0.10 mol·L⁻¹</td>
<td>24 h</td>
<td>25°C</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75-90 μm</td>
<td>1 g/80 mL</td>
<td>NaOH 0.10 mol·L⁻¹</td>
<td>24 h</td>
<td>25°C</td>
<td>[21]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>425-600 μm</td>
<td>10 g/80 mL</td>
<td>NaOH 6 %</td>
<td>48 h</td>
<td>25°C</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 mm</td>
<td>-</td>
<td>NaOH 0.5 mol·L⁻¹</td>
<td>24 h</td>
<td>-</td>
<td>[23]</td>
<td></td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>&lt;1 mm</td>
<td>1 g/20 mL</td>
<td>NaOH 0.1, 0.25 and 0.5 mol·L⁻¹</td>
<td>1 h</td>
<td>90°C</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>carbonization</td>
<td>0.30-0.45 mm</td>
<td>4 g/100 mL</td>
<td>Deionized water</td>
<td>1 h</td>
<td>170-280°C</td>
<td>[25]</td>
<td></td>
</tr>
</tbody>
</table>
The process of obtaining bio-based materials generates acid, neutral and alkaline wastewater. In most of the studies dedicated to bio-based materials, the parameters of this wastewater are not studied, and there are no proposed methods for its treatment.

The purpose of this work is to study the influence of various processing methods in the chemical compositions of bio-based materials from rice husk and wastewater generated. In addition, this work presents the results of wastewater treatment using Fenton-like catalyst based on biogenic silica from rice husk.

2. Materials and Methods

The object of the study is rice husk (*Oryza sativa* L.) of the Dolinny variety of the Far Eastern selection, created at the A. K. Chaika Federal Research Center for Agrobiotechnology of the Far East (Primorskiy Kray, Russia). Rice husk (RH) was sifted through a sieve (particle size 2 mm) to remove small fractions (impurities, dust). Then raw materials were washed with distilled water and dried in air at a temperature of 25°C.

2.1. Obtention process of bio-based materials from rice husk.

The obtention process of bio-based materials from RH included five stages (Figure 1). At the first stage, RH was washed with distilled water; at the second stage it was dried; at the third - dry RH was crushed in a rotary mill and sieved through a 1 mm sieve. At the fourth stage, RH was processed with different solutions: sodium hydroxide 0.5; 0.25; 0.1 mol·L⁻¹ (obtained bio-based materials were named RH–OH–1, RH–OH–2 and RH–OH–3, respectively), different acids – 0.1 mol·L⁻¹ HCl, H₂SO₄, H₃PO₄ solutions (obtained bio-based materials were named RH–H–1, RH–H–2 and RH–H–3, respectively) and distilled water (RH–H₂O). At the last stage, the wastewater formed during the processing of RH was treated using Fenton-like catalysts under conditions of visible and solar light irradiation (heterogeneous Photo-Fenton process).

![Figure 1](https://nanobioletters.com/) Functional scheme of the obtaining process of bio-based materials from rice husks.

2.1.1. Rice husk processing stage.

RH was processed with different acid solutions, sodium hydroxide of different concentrations, or distilled water, as shown in Figure 2. The dosage of the sorbent mass to the volume of the solution was 1 g per 20 mL. Processing was carried out at 90°C for 1 hour with continuous stirring. The processed RH was filtered and washed with distilled water to neutral pH. Then bio-based materials were dried at 80°C to a constant mass.
2.1.2. Stage of wastewater treatment by the photo-Fenton process.

After obtaining bio-based materials, wastewater was treated (Figure 3). At the first stage of treatment, the pH was adjusted to 6 with solutions of HCl (0.1 mol·L⁻¹) or NaOH (0.1 mol·L⁻¹). At the second stage, a heterogeneous photo-Fenton process was carried out using iron-containing Fenton-like catalysts. The catalyst dosage was used at the rate of 1 g of catalyst per 1 L of wastewater. The concentration of hydrogen peroxide was 0.15 mol L⁻¹. The degradation process was carried out at 25°C for 3 hours under visible irradiation with an LED light lamp (power 35 W, color temperature 4100 K, maximum radiation at λ=550-650 nm). The solution was irradiated with constant stirring on a magnetic stirrer for 3 hours. Then the process was continued without stirring in sunlight on sunny days between 9 am and 8 pm in April for 6 days at 25°C. The wastewater formed during the processing of RH-OH-3 sample was previously diluted twice.

2.2. Chemical composition of bio-based materials.

Determination of the chemical composition of bio-based materials from rice husk (RH, RH–H–1, RH–H₂O, RH–OH–3) and initial RH was carried out according to [26].

2.2.1. Substances soluble in cold water.

A conical flask was placed 1 g of dry bio-based materials or RH with 150 cm³ of distilled water at 23 ± 2°C. The mixture was kept at this temperature for 48 hours with periodic stirring. The suspension was filtered. Then, the filter with the remaining sample was dried at a temperature of 103±2°C to a constant mass. The mass fraction of substances soluble in cold water (E) was calculated by the equation (1):

\[ E = \frac{g - (m_1 - m)}{g} \times 100, \]  

where \( m_1 \) – mass filter with the remaining sample, g; 
\( m \) – mass filter, g; 
\( g \) – mass sample, g.
2.2.2. Substances soluble in hot water.

For determining substances soluble in hot water, 1 g of sample was placed into a conical flask and filled with 50 cm$^3$ of distilled water. A reverse refrigerator was attached to the flask and placed into a boiling water bath. Extraction was carried out for 3 hours. After that, the suspension was filtered. Then, the filter with the remaining sample was dried at 103±2°C to a constant mass. The mass fraction of substances soluble in hot water was calculated using equation (1).

2.2.3. The content of pentosans by a modified bromide-bromate method.

1 g of a sample was placed into a distillation flask with 100 cm$^3$ of HC1 12%. The flask must have a label corresponding to the specified volume of acid. The distillation flask was connected to a drip funnel and a refrigerator. The flask was heated by an electric flask heater. The distillate receiver with a capacity of 500 cm$^3$ was placed into an ice bath. During distillation, the tap of the drip funnel was installed so that with the continuous addition of acid into the distillation flask, a constant initial level was maintained. The distillation was carried out until 300 cm$^3$ of distillate was obtained. Next, the distillate was transferred to a flask with a capacity of 1 L. The distillate residues from the receiver were washed off with 50 cm$^3$ of distilled water, and 250 g of crushed ice prepared from distilled water was added into a flask with the distillate. After reducing the temperature of the contents of the flask to 0°C, 20 cm$^3$ of a bromine-bromate solution 0.2 mol·L$^{-1}$ (KBr+1/5KBrO$_3$) were added from the burette and then mixed. The flask was closed with a stopper, and the reaction mixture was left standing for 5 minutes. Then 10 cm$^3$ of a 10% KI solution was added, the flask was again closed with a stopper and shaken to absorb bromine vapors. The released iodine was titrated with a sodium thiosulfate solution with a concentration of 0.1 mol·L$^{-1}$ with starch as an indicator. In parallel, a control titration was carried out, in the same way, using a mixture of 270 cm$^3$ of a 12% HCl solution and 80 cm$^3$ of distilled water. The mass fraction of pentosans was calculated by the equation (2):

$$P = \frac{0.0075(a-b)}{g} \cdot 100 - 1.0, \quad (2)$$

where $a$ – volume of sodium thiosulfate solution with a concentration of 0.1 mol·L$^{-1}$ for control titration, cm$^3$;

$b$ – volume of a solution of sodium thiosulfate with a concentration of 0.1 mol·L$^{-1}$ for the titration of the distillate, cm$^3$;

$g$ – dry mass sample, g;

factor 0.0075 = 0.0048 1.375/0.88, where 0.0048 is the mass of furfural in g, corresponding to 1 cm$^3$ of sodium thiosulfate solution with a concentration of 0.1 mol·L$^{-1}$, 1.375 is the theoretical conversion coefficient of furfural to pentosans, 0.88 is a correction for incomplete furfural yield from pentosans.

2.2.4. Lignin content.

The lignin content was determined with 72% sulfuric acid in the Komarov modification. 1 g of sample was placed into a flask with a capacity of 50 cm$^3$. The suspension was added 15 cm$^3$ of 72% H$_2$SO$_4$ (density 1.64 g/cm$^3$) and kept in a thermostat at a temperature of 24-25°C for 2.5 hours with periodic careful stirring. Then the mixture of lignin and acid was transferred to a conical flask with a capacity of 500 cm$^3$, mixture residues were washed off with 200 cm$^3$
of distilled water and added into a conical flask. The diluted mixture was boiled (low boiling) with a reverse refrigerator on an electric stove for 1 h. Then lignin was filtered through a porous glass filter. Next, the filter with lignin was dried at 103±2°C to a constant mass. The mass fraction of lignin was calculated by the equation (3):

\[ L = \left( \frac{m_1 - m}{g} \right) - 100, \]  

where \( m_1 \) – mass filter with lignin, g; 
\( m \) – mass filter, g; 
\( g \) – mass sample, g.

2.2.5. Cellulose content.

The cellulose content was determined using a nitrogen-alcohol method. For the analysis, a nitrogen-alcohol mixture consisting of one volume of concentrated nitric acid (density 1.4 g/cm\(^3\)) and four volumes of 95% ethanol solution was used.

1 g of a sample was placed into a conical flask of 250 cm\(^3\) and 25 cm\(^3\) of a nitrogen-alcohol mixture was added. A reverse refrigerator was attached to the flask, and the sample with the mixture was boiled in a water bath for 1 hour. After the end of boiling, the liquid was filtered. The sample on the filter was washed back into the flask, using 25 cm\(^3\) of a fresh nitrogen-alcohol mixture, and boiled again in the flask with a reverse refrigerator for 1 hour. This process was carried out five times. After the last process, the cellulose was filtered, washed with 10 cm\(^3\) of a fresh nitrogen-alcohol mixture, and then hot water. The acid washing was checked by the methyl orange indicator. The filter with cellulose was dried at 103±2°C to a constant weight. The mass fraction of raw cellulose was calculated using the equation (4):

\[ C = \frac{m_1 - m}{g} \cdot 100, \]  

where \( m_1 \) – mass filter with cellulose, g; 
\( m \) – mass filter, g; 
\( g \) – mass sample, g.

2.2.6. The content of easily hydrolyzable polysaccharides.

Into a conical flask with a capacity of 250 cm\(^3\) was placed 2.5 g of sample and 100 cm\(^3\) of 2% HCl and boiled with a reverse refrigerator on an electric stove for 3 hours. After the hydrolysis was completed, the sample was filtered. The residue on the filter was washed with hot water until a negative reaction to the acid according to a methyl orange indicator and then used to determine difficult hydrolyzable polysaccharides. The filtrate and washing water were transferred to a measuring flask with a capacity of 250 cm\(^3\); the solution was then brought with distilled water to the mark and then mixed. The mass fraction of reducing substances (RS) as a percentage was determined in the resulting solution (see section 2.2.8). The mass fraction of easily hydrolyzable polysaccharides was calculated by the equation (5):

\[ X_e = \frac{c \cdot V \cdot k_1}{g \cdot 100} \cdot 100, \]  

where \( c \) – mass fraction of RS in the hydrolysate of easily hydrolyzable polysaccharides, %; 
\( V \) – volume of hydrolysate (250 cm\(^3\)); 
\( k_1 \) – conversion coefficient of monosaccharides to polysaccharides (0.88); 
\( g \) – mass of the sample, g.
2.2.7. The content of difficult hydrolyzable polysaccharides.

The remainder of the sample after hydrolysis of easily hydrolyzable polysaccharides and washing was quantitatively transferred from the filter to a glass with a capacity of 100 cm$^3$ and dried at 50-60°C, then 20 cm$^3$ 80% H$_2$SO$_4$ was added and stayed at a room temperature for 3 hours with a periodical stirring. The mixture was quantitatively transferred into a conical flask with a capacity of 500 cm$^3$, washed off with distilled water in an amount of 300 cm$^3$. The flask was connected to a reverse refrigerator and boiled on an electric stove for 3 hours. After the hydrolysis was completed, the solution was filtered. The residue on the filter was washed with small portions of hot water until a negative reaction to the acid according to the methyl orange indicator. The filtrate and washing water were transferred to a measuring flask with a capacity of 5000 cm$^3$. After cooling, the volume of the solution was brought to the mark with distilled water. The concentration of RS was determined in the neutralized solution (see section 2.2.8). The mass fraction of difficult hydrolyzable polysaccharides was calculated by the equation (6):

$$X_h = \frac{c_m \cdot V \cdot n \cdot k_h}{g \cdot 100} \cdot 100,$$

(6)

where $c_m$ – mass fraction of RS in dilute neutralized hydrolysate, %; $V$ – total volume of acid hydrolysate (500 cm$^3$); $n$ – dilution of the hydrolysate during neutralization ($n = 2$); $k_h$ – conversion coefficient of monosaccharides to polysaccharides (0.90); $g$ – mass sample, g.

2.2.8. Mass fraction of reducing substances in hydrolysates according to the method of Maken and Shoorl.

To obtain the Fehling reagent, two solutions were prepared: A – 69.3 g of CuSO$_4$ · 5H$_2$O in 1 L of distilled water; B – 346 g of seignette salt and 100 g of NaOH in 1 L of distilled water. Into a conical flask with a capacity of 250 cm$^3$ was added 5 cm$^3$ of solution A, 5 cm$^3$ of solution B, and 10 cm$^3$ of hydrolysate of easily hydrolyzable polysaccharides or neutralized hydrolysate of difficult hydrolyzable polysaccharides. The mixture was diluted to 25 cm$^3$ and then mixed. Then the mixture was heated up to a boil for 3 minutes and boiled for 2 minutes. At the end of boiling, the flask was quickly cooled, a solution of KI (3 g of KI in 10 cm$^3$ of water) and 5 cm$^3$ of a 25% H$_2$SO$_4$ solution were added, and released iodine was immediately titrated with a solution of sodium thiosulfate with a concentration of 0.1 mol·L$^{-1}$ with starch as an indicator. A control experiment was carried out under similar conditions but without the addition of a sugar solution. According to the difference in the consumption of the Na$_2$S$_2$O$_3$ solution in the control and experiments, the amount of sugar in the hydrolysate sample was determined using the empirical table given in [26]. The mass fraction of RB in the hydrolysates was calculated by equation (7)

$$c = \frac{b \cdot 100}{V \cdot 100} \cdot 100,$$

(7)

where $b$ – amount of sugar in the hydrolysate sample by volume V (20 or 10 cm$^3$), in the empirical table according to [26], mg.
2.2.9. Determination of the mass fraction of moisture.

The mass fraction of moisture was determined as follows: approximately 1 g of sample was put into a crucible. The crucible with the sample was placed into a drying box preheated to 105–110°C and dried for 1 h. Then, the crucible with the sample was removed from the drying box, cooled in a desiccator, and then weighed. The weight proportion of water (% moisture) in the samples was calculated as a percentage by the equation (8):

\[
\% \text{ moisture} = \frac{m_1 - m_2}{m_1 - m} \cdot 100,
\]

where \( m \) – mass of the sample, g;
\( m_1 \) – weight of the crucible with the sample before drying, g;
\( m_2 \) – weight of the crucible with the sample after drying, g.

2.2.10. Ash content determination.

Determination of loss on ignition was performed by the following procedure. About 1 g of the sample was placed into two crucibles each. Crucibles with the samples were placed into a muffle furnace, and the samples were gradually calcinated over 2–2.5 h at (800–850°C). Then the crucibles were cooled first in the air for 5 min and then in a desiccator, and then they were weighed. The loss on ignition (% ash content) was calculated at a percentage by the equation (9):

\[
\% \text{ ash content} = \frac{m \cdot 100}{m_1 \cdot (100 - X_1)} \cdot 100,
\]

where \( m \) – mass of residue after calcination, g;
\( m_1 \) – mass of the sample before calcination, g;
\( X_1 \) – moisture content in the test sample, %.

2.3. Wastewater composition.

The study of the chemical composition of wastewater was carried out according to the main hydrochemical indicators: pH, color, turbidity, chemical oxygen demand (COD), and phenolic content. These indicators were determined before and after the wastewater treatment process. pH was determined using the FiveEasyPlus 20 pH meter (Mettler Toledo, Switzerland); color and turbidity were determined using the UNICO-1201 spectrophotometer (United Products & Instruments Inc., USA).

2.3.1. Chemical oxygen demand.

Measurements of COD were carried out by a method based on the treatment of a water sample with sulfuric acid and potassium dichromate at 150±5°C in the presence of a silver sulfate oxidation catalyst and by the addition of mercury(II) sulfate, which was used to reduce the effect of chlorides. The COD value was determined on a precalibrated Fluorat-02 fluid analyzer (Lumex, Russia). While calibrating the analyzer and all measurements in the range from 10 to 160 mgO·L−1, we used a light filter at a wavelength (440±20) nm in the excitation channel.
2.3.2. Phenolic content determination.

The polyphenols were determined photometrically using the Folin reaction with the phenolic reagent Folin-Ciocalteu. A phenol solution in water was used as the standard solution for the determination of the polyphenols. The optical density of the solution was determined on a UNICO-1201 spectrophotometer at a wavelength of 650 nm. A blank sample was used as a reference solution [27].

2.4. Degradation of phenol using a heterogeneous photo-Fenton process.

In this study, the iron-containing Fenton-like catalysts SiO₂-Fe-300 [28] and RH-Fe-300 catalysts [29] we obtained in previous studies were used. An aqueous solution of phenol was used as a model system. The concentration of phenol (pH ~ 6.3) in the solution was 1006 mg·L⁻¹. The degradation of phenol was carried out under the same conditions as wastewater treatment (see section 2.1.2).

3. Results and Discussion

3.1. Yield of bio-based materials from rice husk.

In this study, seven bio-based materials were obtained according to the schemes shown in Figures 1 and 2. The table shows the yield of bio-based materials processed by different methods. Minimal loss of biomass was in the sample subjected to the simplest processing with distilled water. Processing of the RH by acids promotes the extraction of polysaccharides from the biomass. For bio-based materials processed by acids, results show that yield % doesn’t depend on the acid type. The lowest bio-based materials yield was by alkali processing (NaOH), and the yield % decreases from 78% to 59% with an increase of sodium hydroxide concentration. The lost mass from rice husk can be explained by the partial dissolution of lignin, polysaccharides, and amorphous silicon dioxide in an alkaline medium.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH–H₂O</td>
<td>89±3</td>
</tr>
<tr>
<td>RH–OH–1</td>
<td>59±5</td>
</tr>
<tr>
<td>RH–OH–2</td>
<td>64±4</td>
</tr>
<tr>
<td>RH–OH–3</td>
<td>78±5</td>
</tr>
<tr>
<td>RH–H–1</td>
<td>87±2</td>
</tr>
<tr>
<td>RH–H–2</td>
<td>83±5</td>
</tr>
<tr>
<td>RH–H–3</td>
<td>85±3</td>
</tr>
</tbody>
</table>

3.2. Characteristics of bio-based materials from rice husk depending on the processing method.

The chemical composition of bio-based materials and the initial RH are shown in Table 3. Substances soluble in cold and hot water are more in RH than in bio-based materials because they were removed during processing by water, acid, and alkali [30]. The lowest content of easily hydrolyzable polysaccharides is in the bio-based materials processed by acid because polysaccharides are well hydrolyzed in hydrochloric acid. The main part of the difficult hydrolyzable polysaccharides is cellulose, which is not destroyed by the processing of RH by water, acid, or alkali, so the content of difficult hydrolyzable polysaccharides in the samples is practically the same. The results of easily and difficult hydrolyzable substances of RH obtained in this work are according to [31], showing 18% of easily hydrolyzable and 29% of difficult...
hydrolyzable polysaccharides. As shown in Table 3, the lowest content of pentosans was found in the sample processed by acid due to the conversion of pentosans into pentoses under the action of hydrochloric acid [32]. The pentosan content in the bio-based materials RH, RH–OH–3, and RH–H2O is 17-22%, according to [33] rice husk without processing contains 16-22% of pentosans. Sodium hydroxide is usually used for solubilization and extraction of lignin from biomass, acting on the acetyl group in hemicellulose and connecting lignin with carbohydrate components. However, this processing does not significantly break the aromatic structure of lignin. Rice husk contains about 36% cellulose. The amount of cellulose increases during alkaline processing since lignin and hemicellulose are unstable with alkaline reagents [34]. In addition, the percentage of cellulose increases from 36 to 47% after alkaline processing due to the removal of silica [35].

Table 3. Chemical composition of bio-based materials, %.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Substances soluble in cold water</td>
<td>7.5</td>
<td>0.3</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Substances soluble in hot water</td>
<td>13.1</td>
<td>4.3</td>
<td>5.8</td>
<td>5.7</td>
</tr>
<tr>
<td>Easily hydrolysable polysaccharides</td>
<td>17.7</td>
<td>8.4</td>
<td>13.6</td>
<td>17.2</td>
</tr>
<tr>
<td>Difficult hydrolysable polysaccharides</td>
<td>29.1</td>
<td>28.1</td>
<td>28.4</td>
<td>28.8</td>
</tr>
<tr>
<td>Pentosan</td>
<td>16.6</td>
<td>15.2</td>
<td>18.5</td>
<td>22.3</td>
</tr>
<tr>
<td>Lignin</td>
<td>38.6</td>
<td>33.8</td>
<td>37.4</td>
<td>48.6</td>
</tr>
<tr>
<td>Cellulose</td>
<td>36.4</td>
<td>40.1</td>
<td>39.3</td>
<td>47.3</td>
</tr>
<tr>
<td>Moisture</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Ash content</td>
<td>16</td>
<td>19</td>
<td>16</td>
<td>9</td>
</tr>
</tbody>
</table>

The moisture of RH and bio-based materials is less than 10 %. The ash content of rice husk is 16 %, which is consistent with the literature [36]. The highest ash content in the sample of RH–H–1 is due to the residual content of hydrochloric acid; the lowest result was obtained for RH–OH–3 because organic substances and silica are removed during alkaline processing.

3.3. Wastewater treatment using iron-containing Fenton-like catalysts.

Wastewater, formed during the processing of bio-based materials, was treated according to the scheme shown in Figure 3. The iron-containing composites RH-Fe-300 [28] and SiO2-Fe-300 [29] based on biogenic silica were used as photo Fenton-like catalysts in the degradation reaction of phenolic aqueous solutions with neutral pH value under the visible and solar irradiation. The results of the degradation reaction of phenol are given in Figure 4. The figure shows that the process of phenol degradation proceeds better in the presence of the RH-Fe-300 catalyst. The concentration of phenol using RH-Fe-300 decreases from 1006 to 0.5 mg L⁻¹ for 72 hours, while using SiO2-Fe-300 from 1006 to 324 mg L⁻¹. The concentration of phenol without catalyst doesn’t change with time. During the process with the RH-Fe-300 catalyst, iron(III) cations are slightly leached into the reaction solution. These results can be explained by the fact that iron is well dispersed in the silica matrix and is chemically bound to it in the form of a Si-O-Fe silicate structure [29]. The SiO2-Fe-300 sample is more susceptible to photo corrosion in aqueous solutions of phenol (Table 4). Thus, RH-Fe-300 is a preferable catalyst for the degradation of phenol in aqueous solutions. Therefore, the RH-Fe-300 catalyst was chosen to treat wastewater generated during the production of bio-based materials. It is important to note that previous studies [37, 38] showed that lignin-containing solutions are sufficiently stable in time by different irradiation without using catalyst because they contain very strong organic compounds.
Table 4. Iron (III) cations content in the solutions after degradation of phenol process.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fe (mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH-Fe-300</td>
<td>3.55</td>
</tr>
<tr>
<td>SiO₂-Fe-300</td>
<td>14.05</td>
</tr>
</tbody>
</table>

Figure 4. Kinetic curves of changes in the concentration of phenol using Fenton-like catalysts.

The composition of wastewater generated during the obtention of bio-based materials before and after treatment using a Fenton-like catalyst RH-Fe-300 in the presence of H₂O₂ under visible and solar irradiation is shown in Table 5. Wastewater formed after acid, alkaline and water processing (W–RH–H–1, W–RH–H₂O and W–RH–OH–3, respectively) is characterized by high values of color, turbidity, COD, and the content of phenolic compounds. During the treatment process, the content of phenolic compounds was controlled over time. Figure 5 shows that the concentration of phenolic compounds slightly decreases after 3 hours and principally decreases after 120 hours, and then the degradation process practically doesn’t occur. After wastewater treatment, all quality indicators decrease depending on the type of processing. The degree of reduction is turbidity – 71-99%, color – 71-98%, COD – 25-28%, the content of phenolic compounds – 35-64% (Table 5). The obtained results show that the lowest efficiency was observed for COD, which characterizes the content of organic compounds. The resulting wastewater is a mixture of difficult-to-decompose organic compounds, consisting mainly of polysaccharides, phenolic compounds, and low-molecular lignin.

Table 5. Wastewater quality indicators before and after treatment.

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>pH</th>
<th>Turbidity (mg·L⁻¹)</th>
<th>Color (degree)</th>
<th>COD (mgO₂·L⁻¹)</th>
<th>The content of phenolic compounds (mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Before</td>
<td>After</td>
<td>Before</td>
</tr>
<tr>
<td>W–RH–H–1</td>
<td>1.3</td>
<td>13</td>
<td>7462</td>
<td>154</td>
<td>6350</td>
</tr>
<tr>
<td>W–RH–H₂O</td>
<td>6.8</td>
<td>~6</td>
<td>663</td>
<td>189</td>
<td>7923</td>
</tr>
<tr>
<td>W–RH–OH–3</td>
<td>11.1</td>
<td>1795</td>
<td>20000</td>
<td>1769</td>
<td>18875</td>
</tr>
</tbody>
</table>
Figure 5. Kinetic curves of changes in the content of phenolic compounds in wastewater formed during the obtention of bio-based materials using the RH-Fe-300 catalyst: (a) W-RH–H–1 and W-RH–H2O; (b) W-RH–OH–3.

4. Conclusions

Seven samples of bio-based materials based on rice husk were obtained due to processing raw materials by various solvents (alkali, acids, and distilled water). These bio-based materials are lignocellulose biomass, which contains substances soluble in water, pentosanes, lignin, cellulose, easily and hardly soluble polysaccharides. The chemical composition of bio-based materials depends on the rice husk processing method. After alkali processing, bio-based materials contain mainly cellulose; after acid processing contains lignin and cellulose with less easily hydrolyzable polysaccharides. Water treatment of rice husk does not change its chemical composition. All generated wastewater is characterized by high values of color, turbidity, COD, and the content of phenolic compounds. It was established that after wastewater treatment using Fenton-like catalyst RH-Fe-300 under visible and solar irradiation, the color, turbidity, and phenolic compounds decrease by 71-99%, 71-98%, and 35-63%, respectively, while the reduction of COD did not exceed 30%.

Funding

This research received no external funding.
Acknowledgments

This research has no acknowledgment.

Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study, in the collection, analysis, or data interpretation, in the writing of the manuscript, or in the decision to publish the results.

References


