

The effects of pH on the precipitation of rice straw lignin from An Giang, Vietnam

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Received 7 July 2021; revised 21 September 2021; accepted 5 October 2021

Abstract:

This research aimed to extract lignin from rice straw and reveal the pH value of diluted acid at which the most effective yield of lignin was precipitated. In this study, rice straw obtained from local fields in the An Giang province of Vietnam and sodium hydroxide 2 M was employed to extract lignin from rice straw. Hydrochloric acid was used to adjust the sample pH values to be in the range of 1.5-3.5. Fourier-transform infrared spectroscopy (FTIR) analysis was used to characterize the functional groups of the lignin materials. Thermogravimetric analysis (TGA) analysis was employed to supply information on the thermal decomposition of the lignin samples. Herein, the results showed that lignin precipitated at different pH values affected its thermal properties. At 700°C, the yield of the remaining lignin components were 56% at pH 2.0, but the weight loss of lignin samples precipitated at pH 3.5 dropped to 85% because many non-lignin substances existed in the samples. The yield of the crude lignin samples obtained were 16.51, 17.66, 15.27, 14.33 and 13.26% for pH of 1.5, 2.0, 2.5, 3.0 and 3.5 respectively. The crystallite regions played an important role in the lignin structures. The spectrum peaks at pH 1.5, 2.0 and 2.5 were broader than the peaks at pH 3.0 and 3.5. The results demonstrated the highest percentage of lignin precipitate was collected at pH 2.0.

Keywords: agglomerate, crystallinity region, decomposition, lignin, precipitate, redissolve, rice straw, thermal.

Classification number: 2.2

1. Introduction

Lignin is an aromatic organic polymer composed of three precursor aromatic alcohols, namely, p-coumaryl, syringyl, and guaiacyl [1, 2]. With an amorphous structure, lignin performs the function of plant cell binding and cell wall void filling along with cellulose, hemicellulose, and pectin [3]. Lignin does not exist as an independent polymer in plant cells but is always bound to carbohydrates (i.e., hemicellulose) to form lignin-carbohydrate complexes [2]. Due to stable binding with many functional groups, lignin is widely found in resins, emulsifiers, dyes, paints, asphalt, nutrients, and synthetic fuels [4, 5].

As a natural complex organic polymer with wide applications in many fields, lignin can be extracted by various methods depending on source material types (mainly herbaceous) and lignin-chemical structure [2]. The first lignin-carbohydrate complex was successfully extracted with hot water in 1953 [2, 6]. After that, organic solvents, alkaline solutions, acids, enzymes, microbiological methods, and ultrasonic treatments were tested toward the improvement

of lignin purity and recovery [2-5]. Among those methods, alkaline hydrolysis is proven to be a promising approach that is non-toxic to the environment and has a high lignin recovery rate [1, 4]. In this approach, α -ether bonds between lignin-hemicellulose and ester bonds (between lignin-hemicelluloses and hydroxycinnamic acids) are broken such that the lignin can be separated from the alkaline soluble complex mixture [1, 2]. More importantly, acids are also believed to have an essential influence on lignin precipitation from soluble mixtures with non-lignin components [2, 7]. However, when the concentration of H^+ is too high, the decomposition coefficient of lignin will increase, whereas, a low concentration of H^+ will affect the structure of the obtained lignin because the non-lignin components are not completely separated [7]. The differences in these structures of lignin can be examined by the following methods: FTIR spectroscopy, TGA, and X-ray diffraction analysis (XRD) [1, 4]. Therefore, to recover lignin from herbaceous plants, alkaline hydrolysis is considered efficient but depends upon acid concentration and lignin structure [1, 4, 7].

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Raw materials for lignin extraction are diverse and include all woody plants of which the most important are herbaceous plants because of their abundance. Rice straw, an agricultural waste, is also considered an abundant lignin source due to it consisting of the three main carbon-rich components, namely, cellulose (32-47%), hemicellulose (19-27%) and lignin (5-24%) [8]. Approximately 370-520 million tons/year of this biomass source is generated globally of which Vietnam generates approximately 50 million annually [9, 10]. Furthermore, much of this biomass source is currently wasted due to policies allowing open burning, which causes air pollution [9].

In this study, various pH values were tested (using alkaline extraction) to determine which pH values would obtain a high yield of precipitated lignin. Then, the characteristics of the crude lignin were investigated using XRD, FTIR and TGA.

2. Materials and methods

2.1. Materials

Rice straw was obtained from local rice fields in An Giang Province, Vietnam. The rice straw was washed in deionized water to remove impurities [11] and troublesome elements like insect larvae, dust, soil, etc. After that, the rice straw was sun-dried to reduce its moisture content to 4-5.5% and was then chopped into lengths of 1-2 cm. The dry sample was ground to a fine powder using a commercial blender (DFY-2000, Vietnam), and then sieved to the size of 0.08 mm to achieve the so-called dried rice straw (DRS). The DRS was stored in sealed polyethylene bags at ambient temperature for future use. Then, 150 g of cleaned rice straw/DRS was mixed with 3600 ml of acetone 5% to remove oils, pigments, and wax [12, 13] to obtain dewaxed DRS.

The chemicals used for lignin extraction consisted of perchloric acid, hydrochloric acid, toluene, ethanol, and sodium hydroxide, which were obtained from Merck, Germany.

2.2. Methods

In this study, a chemical method was used to extract lignin from rice straw. Fifty grams of the dewaxed DRS was added to 1000 ml of NaOH 2 M [5, 14]. This mixture was sonicated in a S100-Elmasonic (Germany, 37 kHz) ultrasonic bath for 30 min at 90°C. Then, it was refluxed at 90°C for 90 min. After that, it was cooled to 40°C and filtered to remove residual biomass [15]. Hydrochloric acid 6 M was added into the filtrate until the pH reached 4.0, then it was stored at 4°C for 24 h. Next, three volumes of ethanol 95% were added to the liquid and kept at 4°C for 6 h for hemicellulose coagulation. Hemicellulose precipitates and the filtrate were obtained by vacuum suction. Ethanol was

recovered and the liquid containing lignin was obtained. According to the research of M.A. Hubbe, et al. (2019) [16], the hydroxycarboxylic acids in lignin molecules can become less soluble forms when pH is decreased to below 3.5. Therefore, to optimize lignin precipitates from the filtrate, the liquid's pH was adjusted from 3.5 to 1.5 and the pH values were measured by a pH meter (Extech 407228, USA). The diluted solution of hydrochloric acid 6 M was added to five samples containing 100 ml of the liquid to reach a target pH ranging from 3.5 to 1.5 [17]. All the samples were left for 24 h for lignin precipitation [15]. Each settled sediment was collected by a filter and then dried at 80°C until constant mass [4]. The yield of collected lignin was determined from the difference between the initial weight of the rice straw sample used for lignin extraction and the dried weight of lignin collected.

2.3. Characterisations

FTIR, TGA, and XRD were used to evaluate the fundamental properties of the lignin products. FTIR analysis was conducted with an Alpha-Bruker FTIR spectrometer using KBr powder to determine the absorbance of the functional groups of lignin, and the measurements were performed in the range of 500-4000 cm^{-1} with a resolution of 4 cm^{-1} [18].

TGA was accomplished on a Q500-TA instrument operating from temperature room (24-28°C) to 700°C with a heating rate of 20°C/min under a nitrogen atmosphere. The TGA presented the change in weight of the lignin samples as a function of temperature. The TGA curves indicated the rate of mass loss versus temperature, which was used to recognize the thermal stability of lignin [15].

The evaluation of lignin crystallinity was carried out using XRD on an Aeris Panalytical Diffractometer with Cu K α Ni-filtered radiation of $\lambda=1.543 \text{ \AA}$ with a working voltage of 45 kV. The diffraction patterns in the 2 θ mode between 10-50° were recorded with a step size of 0.019° and a scan time of 43.00 s/step [15, 19].

2.4. Statistical analysis

All experiments were carried out in triplicate. The paired t-test was performed to determine the statistically significant effect of pH values on lignin yields by using the SPSS package ver. 11-2018 (USA).

3. Results

3.1. The yields of raw lignin at different pH values

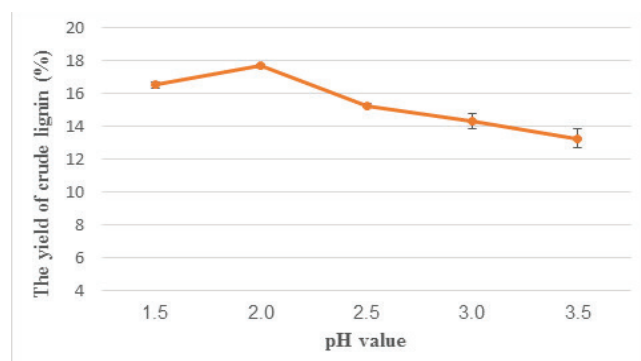
Table 1 shows the paired t-test results of the raw lignin yields that were precipitated with hydrochloric acid at different pH values in the range of 3.5-1.5.

Table 1. The Paired T-test result of raw lignin yields by pH.

Paired samples test	Mean	N	Standard deviation	Significant (2-tailed)
Pair 1	pH1.5	16.51	3	0.16
	pH2.0	17.66	3	0.13
Pair 2	pH1.5	16.51	3	0.16
	pH2.5	15.27	3	0.15
Pair 3	pH1.5	16.51	3	0.16
	pH3.0	14.33	3	0.47
Pair 4	pH1.5	16.51	3	0.16
	pH3.5	13.26	3	0.60
Pair 5	pH2.0	17.66	3	0.13
	pH2.5	15.27	3	0.15
Pair 6	pH2.0	17.66	3	0.13
	pH3.0	14.33	3	0.47
Pair 7	pH2.0	17.66	3	0.13
	pH3.5	13.26	3	0.60
Pair 8	pH2.5	15.27	3	0.15
	pH3.0	14.33	3	0.47
Pair 9	pH2.5	15.27	3	0.15
	pH3.5	13.26	3	0.60
Pair 10	pH3.0	14.33	3	0.47
	pH3.5	13.26	3	0.60

The paired sample t-test was used to assess the statistical difference between the pH values on the mean yields of lignin. The results showed that the pair of pH 2.5-3.0 (pair 8) and the pair of pH 3.0-3.5 (pair 10) were not significantly different ($\text{sig.} > 0.05$) within each pair at a confidence level of 95%. There were significant differences within each pair ($\text{sig.} < 0.05$) at a 95% confidence level. The mean yield obtained varied from 13.26 to 17.66 g.

Figure 1 indicates that the decrease of pH from 3.5 to 1.5 increased the yield. The highest percentage of lignin precipitate was above 17% at pH 2.0. These observations agree with previous studies [15, 19]. The curve was divided into two stages: firstly, when pH was reduced from 3.5 to 2,

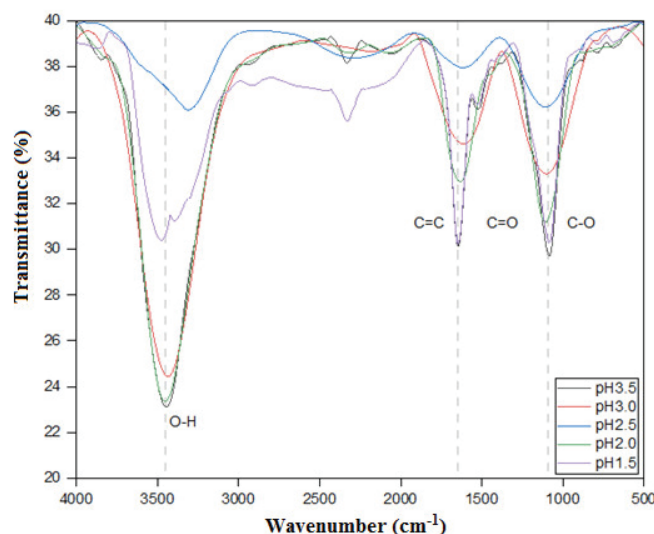
**Fig. 1. The change in yield at different pH values.**

more lignin started to precipitate because the hydrogen ions in the hydrochloric acid solution interacted with the negatively charged lignin molecules. The repulsive forces between suspended particles were reduced and the coagulation of lignin occurred. Thus, a higher concentration of hydrogen ions increased the precipitation of lignin. At pH 2.0, the highest yield was obtained because of the lower amount of soluble carboxyl acids. In the second stage, the yield of lignin precipitation decreased when more hydrochloric acid was added to the mixture because the precipitates became unstable and re-dissolved. According to S. Priyanto, et al. (2019) [7], the higher the concentration of acidity, the easier the lignin coagulation formed. However, if the mixture was too acidic, the lignin yield was potentially damaged. Therefore, the target pH to precipitate lignin was pH 2.0 [15].

4. Characterisations

4.1. FTIR analysis

The spectra of the lignin samples obtained at pH values from 3.5 to 1.5 are analysed using FTIR in the range of 500-4000 cm^{-1} and are shown in Fig. 2. All the spectra show variations in band intensities that are related to the functional groups of lignin. From 3000-3450 cm^{-1} , the broad vibration was assigned to hydroxyl groups and did not correlate with the pH changes of the solutions. The carbonyl groups corresponded to the absorbance at 1650 cm^{-1} , however, there was a significant drop in peaks when the pH values were higher (pH 3.5, pH 3.0). At 1592 cm^{-1} , which are the bands of aromatic skeletal vibrations, there were changes in the peak intensities with a decrease in pH. The other bands related to methoxyl groups were around 1454-1421 cm^{-1} . The absorbance signals between 1305-1090 cm^{-1} show the C=C, C=O, and C-O groups [4, 15].

**Fig. 2. FTIR spectra of crude lignin at different pH.**

4.2. TGA analysis

Figure 3 indicates weight loss occurring as the TGA curves decrease. The degradation temperature of lignin occurred over a wide temperature range, such as between 100 and 700°C, due to lignin being a natural polyphenolic polymer containing various branching [20]. The degradation of rice straw lignin was seen over three stages. In the first stage, weight loss at 30-100°C occurred due to water evaporation in the lignin samples. For the second stage, the degradation of carbohydrate components occurred and released carbon greenhouse gases such as CO, CO₂ and CH₄ at 180-370°C. In this stage, there was a significant change in the slope of the thermal decomposition. The final stage of lignin degradation started above 450°C, but mass loss rates were much smaller than in the second stage [21]. Also, in the final stage, the breakdown of lignin molecules only occurred when the biomass reached the target thermal energy. From pH 3.5 to 1.5, about 44-15% of all crude lignin samples remained at 700°C [15, 20] because there were trends to form chars from the highly condensed aromatic structure of lignin [22]. However, over 75 and 85% of the weight loss were decomposed at pH 3.5 and pH 3.0, respectively and implied the evidence for higher impurities of lignin precipitates.

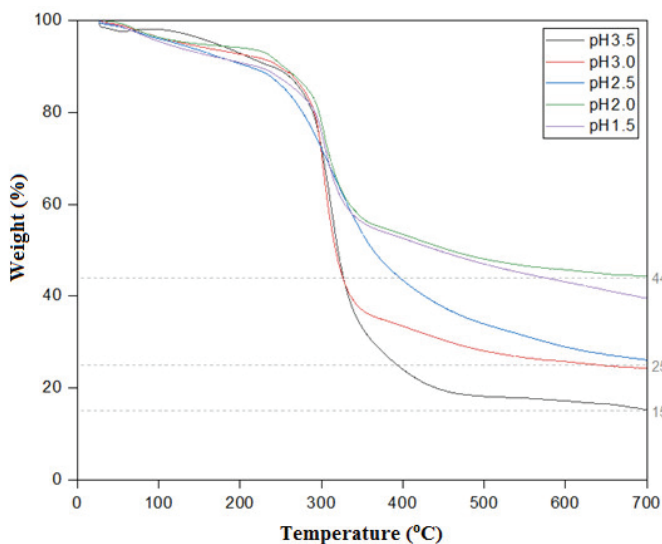


Fig. 3. TGA spectra of crude lignin at different pH values.

4.3. XRD analysis

The XRD analysis in Fig. 4 indicates changes in the crystallinity of lignin samples with pH. At pH values of 3.5 and 3.0, a wide peak at 2θ values ranging from 17 to 32°C is seen, but the lignin peaks obtained at pH 2.5, 1.5, and 2.0 were wider at 2θ from 12 to 38°C. This indicates that the broad peaks are related to the amorphous regions

of the lignin substances. At pH 1.5, the amorphous degree was narrower because of the non-lignin materials in the samples collected [15].

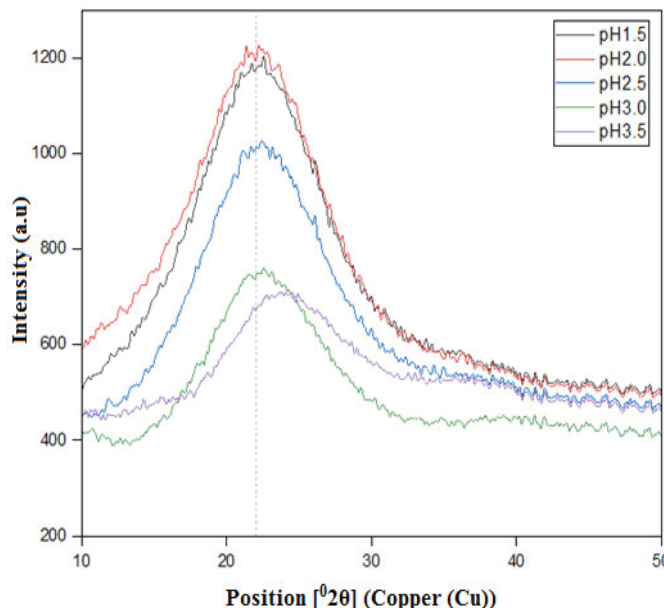


Fig. 4. XRD spectra of crude lignin obtained at different pH values.

5. Conclusions

The study results demonstrated that varying pH values of diluted hydrochloric acid affected lignin yields. The lignin precipitates were 16.51, 17.66, 15.27, 14.33 and 13.26% at pH 1.5, 2.0, 2.5, 3.0, 3.5, respectively. A pH of 2.0 was found to be the most effective to recover crude lignin from the solution. The FTIR spectra showed the most functional groups, such as carbonyl, aromatic rings, and methoxyl. The TGA results indicated that the thermal characteristics of lignin precipitates were related to the change in pH. About 75 and 85% of lignin materials precipitated at pH 3.0 and pH 3.5, respectively, which were thermally decomposed at 700°C. In contrast, 56% of samples at pH 2.0 remained at 700°C because of the condensed aromatic structures of the lignin substances. The XRD analysis indicated that different pH values also significantly affected the crystalline regions of lignin materials. At pH 2.0 and 2.5, the broadened peaks occurred at 2θ from 12 to 38°C, but those became narrower when the value of pH was 1.5.

This paper provides useful information on the efficiency of lignin precipitates from rice straw with respect to pH values. Therefore, it is noted that varying the pH in the lignin coagulation process should be considered and evaluated to obtain the desired lignin mass.

CRediT author statement

Thuy-An Ngo: Conceptualisation, Methodology, Supervision; Dao-Chi Vo Thi, Nhan-Tanh Nguyen Tran, Thien-Khanh Nguyen Tran: Data curation, Software, Visualisation; Minh-Nguyet Doan Thi, Mai-Linh Duong, Lan-Tuyen Nguyen: Investigation, Writing - original draft preparation.

ACKNOWLEDGEMENTS

This research is funded by Vietnam National University - Ho Chi Minh City (VNU-HCM) under grant number "C2020-16-01".

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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