

Research Article

Characterization of Diluted-acid Pretreatment of Water Hyacinth

Auangfa Boontum* and Jirapa Phetsom

Department of Biology, Faculty of Science, Maharakham University, Maha Sarakham, Thailand

Wawat Rodiahwati

Department of Agroindustrial Technology, Sumbawa University of Technology (UTS), Sumbawa, Indonesia

Kanyarat Kitsubthawee

Department of Chemical Engineering, Faculty of Engineer, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

Teerachai Kuntothom

Department of Chemistry, Faculty of Science, Maharakham University, Maha Sarakham, Thailand

* Corresponding author. E-mail: auangfa0809@yahoo.com DOI: 10.14416/j.asep.2019.09.003

Received: 21 August 2019; Revised: 27 August 2019; Accepted: 29 August 2019; Published online: 23 September 2019

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Abstract

Water hyacinth (WH) is an abundant renewable lignocellulosic biomass. The renewable resources are widely studied to produce bioenergy and high value added products. The obstacle of converting the lignocellulosic biomass to products due to its recalcitrant structure, required disruption to enhance the chemical or enzyme accessibility. The aim of this study is to investigate the possibility of WH pretreatment with dilute sulfuric acid (DSA). The addition of sulfuric acid in pretreatment process was varied concentration at 1, 2, 3, and 4% (v/v). The chemical component was analyzed to optimize the pretreatment condition. The results showed that the 2% sulfuric acid had effect on cellulose recovery. The morphological changes of WH due to pretreatment were determined by Scanning Electron Microscopy (SEM). The images showed the destructive surface of all treated samples. The intact surface of native WH was destroyed after pretreatment process while the increment of acid concentration increased the rough surfaces. The Fourier Transform Infrared Spectrometer (FTIR) and X-ray diffraction (XRD) were used for analyzing functional groups and crystallinity, respectively. The FTIR patterns of DSA treated WH were slightly different due to the remained components in samples. The results showed the highest crystallinity index was 55% which was obtained from pretreated WH with 2% sulfuric acid, 80°C, 60 min. In the present study, it was found that DSA pretreatment is possible to modify the chemical structure of WH for developing economical processes.

Keywords: Sulfuric acid, Water hyacinth, Lignocellulosic biomass, Pretreatment, Crystallinity

1 Introduction

Water hyacinth (WH) is aquatic weed originated from the state of Amazon, Brazil [1]. It is a widespread to

rivers and canals in many regions of Thailand. Their spreading is becoming major problems in an aquatic ecosystem due to its rapid growth rate and barrier in water migration, transportation and irrigation channels [2].



The covering of WH blocks the passage of sunlight underwater that effects on growth of other aquatic organism and depletes nutrients and oxygen from water bodies adversely affecting the growth of aquatic species [3]–[5]. WH has been considered as raw materials in many applications such as phytoremediation [6], vermicompost [7], biofertilizer [8], absorbent polymer [9], biofuel as biodiesel [10], [11], biogas [12], bioethanol [13] or etc. WH contains high carbohydrate and low lignin content [14], especially high content of hemicellulose (35–55% of dry weight) [15]. The components are linked together with different covalent and noncovalent bindings to form a complex structure, strong and difficult to break into small molecules under raw condition [16], [17]. The recalcitrant structure of lignocellulosic biomass hinders the hydrolysis and blocks the accessibility of enzymes. Pretreatment is a crucial step to facilitate the separation of hemicellulose, cellulose and lignin and enhances the enzymatic saccharification [18], [5]. The physical structure of biomass can be modified by mechanical pretreatment for size reduction such as grinding, milling and comminution. Nevertheless, the chemical components are still remaining in the biomass, then the combination between chemical and mechanical pretreatment methods is considered to improve the process efficiency [19].

Many pretreatment technologies have been studied on a variety of biomass for efficient, cost-effective and environmentally friendly. To overcome the physicochemical barrier of biomass, pretreatment methods have been studied to reduce the operating costs based on different types of lignocellulosic biomass [20], [21]. The chemical pretreatments using acid and alkaline reagents have been widely studied because of their simplicity and efficient performance [22]. The acid pretreatment methods have advantages compared to other pretreatment methods in term of lignocellulose matrix disruption and amorphous cellulose conversion [23]. The acid pretreatments process is intensively studied in both inorganic and organic acids. However, the organic acid is less attractive due to an unclear mechanism in the pretreatment process [24]. The comparative study on the effect of organic and inorganic acid pretreatment for sugar conversion, reported that the achieved hydrolysis step was not only the acid concentration, temperature, and treatment time, but also the type of acid, differed in the mechanism in pretreatment process [24], [25]. However, the

hypothetical mechanism of organic acid pretreatment has been proposed on the modification of chemical bonding between lignin and carbohydrate, and disintegration of cellulose-hemicellulose fibrils [26]. The new group of organic salts is ionic liquids (ILs) that have been used in various lignocellulosic biomasses such as rice straw [27], water hyacinth [28], sawdusts [29], or sugarcane bagasses [30]. IL has potential in disruption the recalcitrant structure while preserving the cellulose fraction [31] and altering the crystalline to amorphous structure [32].

Due to high hemicellulose and low lignin contents in WH, acid pretreatment is especially suitable for hemicellulose removal from lignocellulosic components [33]–[35]. The loosening matrix of lignocellulosic structure can increase the porosity and improve enzymatic hydrolysis [36]. Dilute sulfuric acid pretreatment is generally referred to hydrolyze cellulose and hemicellulose by using acid as catalyst [35], to increase the solubility of hemicellulose and, to disrupt the chemical bonding between lignocellulosic components [37], [38]. The uses of dilute sulfuric acid have been reported in different lignocellulosic biomasses under high temperature, such as extracted olive oil (170, 190, and 210°C) [39], switchgrass (150 and 160°C) [40], rice straw (169–190°C) [41], cassava (160–200°C) [42], rapeseed straw (180°C) [43]. Releasing sugars of hemicellulose under high temperature lead to degrade to furfural and hydroxymethyl furfural, regarding as strong inhibitors to microbial fermentation [44], [45]. Therefore, the effectiveness of pretreatments depends on the physical structure and chemical composition of the biomass [46].

The aims of this study were to study the native, and DSA treated WH in compositional analysis, characterization of physicochemical changes in different sulfuric acid (H_2SO_4) concentration, reaction time, and temperatures by using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and X-ray diffraction (XRD). As a result, we expected the characteristic changes of DSA treated WH under moderate temperature and low sulfuric acid concentration, leads to optimize the pretreatment process for further value added products.

2 Materials and Methods

2.1 Sample preparation

Fresh WH was obtained from Chee river, located

near Mahasarakham University, Sub-district of Ta Khon Yang, district of Kantarawichai, Maha Sarakham province, Thailand. In this study, we used the stem and leaf of WH which washed thoroughly with tap water after removing roots. The WH was cut into 0.5 to 1.0 cm and dried in oven at 60°C until weight constant. Then, the dried sample was ground and screened through 20 wire-mesh sieve. The sample was stored in an airtight container at room temperature until used.

2.2 Sulfuric acid pretreatment

Pretreatment was performed at different four concentrations of H₂SO₄ (1, 2, 3, and 4% (v/v)) in Erlenmeyer flasks (250 ml) by mixing WH dried powder and H₂SO₄ solution with the ratio 1:10 (w/v). The experiment was studied at different temperatures (60, 80, and 100°C) and incubated reaction in the water bath for 30 and 60 min. After pretreatment, the solid residue was removed by filtration, followed by washing with distilled water and air dried at room temperature. All data were expressed as average (performed as) of duplication experiments.

2.3 Compositional analysis of WH

The composition of cellulose, hemicellulose, and lignin of WH was measured according to Van Soest *et al.* [47]. The biomass recovery rate of the WH samples was calculated according to Equation (1)

$$\text{Biomass recovery rate (\%)} = \frac{[W_{bef}(\text{g}) - W_{aft}(\text{g})] / W_{bef}(\text{g}) \times 100}{(1)}$$

where, W_{bef} and W_{aft} were weight of sample before and after pretreatment, respectively.

2.4 Characterization of native and pretreated WH

2.4.1 Scanning Electron Microscope (SEM)

Surface morphology of samples was observed by SEM (JEOL JSM-6460LV) at an accelerated voltage of 15–20 kV after gold coating by sputtering device (SPI-MODULE, sputter Coater). The samples were coated and mounted on a conductive tape. The morphology of surfaces and pore was monitored and compared with magnification of 1500X.

2.4.2 Fourier-transform infrared spectroscopy (FTIR)

FTIR (PERKIN ELMER) spectroscopy was employed to identify the chemical changes before and after pretreatment. The spectrum was recorded in wave number between 4000 and 400 cm⁻¹ with detector at 4 cm⁻¹ resolution and 25 scan per sample. Samples were prepared by mixing 3 mg of dried sample with 300 mg of KBr (Spectroscopic grade) and subsequently pressed into disks for 3 min at 10 Mpa.

2.4.3 X-ray powder diffraction (XRD)

Crystallinity index of untreated and DSA treated WH was analyzed by XRD diffractometer (Bruker, D-8 Advance). The X-ray diffractograms were recorded in grade range between 10 to 30° (degree) of diffraction angle (2θ) at a scanning speed of 5°/min. The radiation was Cu Kα (λ=1.54 Å) with a step size of 0.03°, 40 KV, 30 mA.

Crystallinity of cellulose was calculated according to the empirical method proposed by Segal's equation [Equation (2)] [48].

$$\text{CrI (\%)} = [(I_c - I_{am})/I_c] \times 100 \quad (2)$$

where, I_c and I_{am} were crystalline and amorphous region, respectively. I_c was measured at 2θ = 22.6°. Meanwhile, I_{am} was determined at 2θ = 18.0°.

3 Results and Discussion

3.1 Compositional analysis of native WH and DSA treated WH

The chemical composition of native or untreated WH is presented in Table 1. and compared with previous reports. The native WH in this study consisted of 22.05% cellulose, 32.60% hemicellulose, and 4.53% lignin. Comparison to the previous reports, the untreated WH had differed contents due to where it originated from [49]. The chemical composition of DSA treated WH is shown in Table 2. These results revealed that the DSA treated WH promoted the hemicellulose releasing and altered the cellulose and lignin contents. The increment of H₂SO₄ concentration above 2% (v/v), the results obtained the lower cellulose and hemicellulose contents. The higher temperature and reaction time caused the

loss of cellulose and hemicellulose contents (data not shown). Singh and Bishnoi [50] and Rezaia *et al.* [51] reported a reduction in the hemicellulose and lignin contents and an increase in the cellulose content of pretreated WH with sulfuric acid. The higher cellulose content caused by disrupting the WH structure by acid [51] while high acid concentration resulted in the loss of polysaccharides [52].

Table 1: The composition of water hyacinth (% w/w)

Cellulose	Hemicellulose	Lignin	References
18.40	49.20	3.55	[55]
19.20	32.69	4.37	[58]
31.67	27.33	3.93	[59]
38.01	24.00	9.50	[22]
32.84	24.70	8.10	[53]
16.40	32.00	5.70	[51]
24.80	30.00	5.60	[60]
22.05	32.60	4.53	This study

Table 2: The composition of water hyacinth (% w/w) after DSA pretreatment

Treatment	Cellulose	Hemicellulose	Lignin
Native	22.05±0.1	32.60±0.3	4.53±0.3
2% H ₂ SO ₄ 60°C, 30 min	24.01±0.4	29.45±0.4	4.41±0.3
2% H ₂ SO ₄ 60°C, 60 min	24.65±0.2	27.70±0.6	4.13±0.2
2% H ₂ SO ₄ 80°C, 30 min	25.85±0.5	25.10±0.1	4.03±0.2
2% H ₂ SO ₄ 80°C, 60 min	26.45±0.5	24.60±0.2	4.01±0.4
2% H ₂ SO ₄ 100°C, 30 min	26.95±0.3	23.45±0.3	3.55±0.3
2% H ₂ SO ₄ 100°C, 60 min	28.45±0.4	22.60±0.2	3.23±0.5

The compositional changes of DSA treated and native WH residues were investigated the effect of temperature and time. The results showed that increasing the temperature had a tendency to increase the cellulose content while the hemicellulose and lignin content slightly decrease. These results agree with previous study that hemicellulose was solubilised by DSA and increase cellulose accessibility without removing much of the lignin from biomass [40]. The compositional analysis revealed that DSA pretreatment at high temperature and long reaction time lead to slightly

higher cellulose recovery than milder conditions.

The DSA pretreatments performed in hot water bath, which facilitated the heat through the materials without losing power. In hot water bath, heat transfer occurs through convection and followed by conduction. The water is the medium of heat transfer that hot water is indirectly contacted with the base of the glassware containing substrate [53]. During thermal pretreatment, lignin is eradicated merely up to a certain limit. However the dissolution and depolymerisation/repolymerisation of lignin reaction creates the redistribution on the fibre surfaces again [54], [55]. Moreover, the quantity of lignin solubilisation is related to its degradation during pretreatment process [56].

The biomass recovery after DSA treated WH at 80°C for 60 min, was observed and found that the recovery percentage was 68, 67, 63, and 62% (w/w) when applying 1, 2, 3, and 4% (v/v) H₂SO₄, respectively. Contrasting to Rezaia *et al.* [51], the recovery percentage was 50, 62, 65, and 58% (w/w) when using 4, 5, 6, and 7% H₂SO₄, respectively. The higher recovery percentage obtained from our study caused by mild-pretreated condition with lower temperature and acid concentration. Xia *et al.* [57] reported the reaction time of pretreatment affected the weight percentage as increasing time from 5 to 45 min caused residual biomass decrease to 22%.

3.2 SEM analysis

The morphological changes in untreated and DSA treated WH were investigated by electron microscopy. The morphology of untreated WH had a well-shaped fibril and smooth intact with a rigid lignin compact structure (Figure 1). Similarly, the previous studies reported a firm and highly organized structure in untreated WH [51], [61]. The observation changes were found in DSA treated WH that the structural surface was rough scaly destructed cellulose matrix and cracked with a few hollows (as shown in Figure 1). The DSA treated WH showed the splitting surface which revealed the loss of matrix and chemical bonding. The comparison of untreated and DSA treated WH found that treated samples were more destroyed with higher acid concentrations. These results confirmed that the acid tended to interact with the cellulose component rather than the lignin in the specific WH structure [51] and loss of the structural integrity [49].

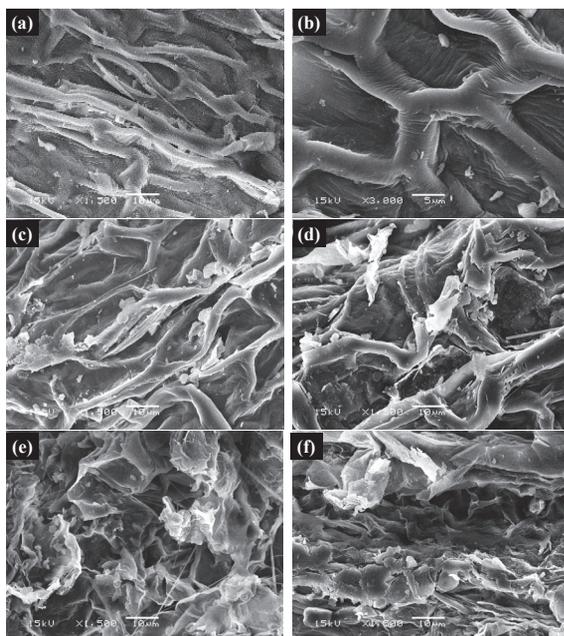


Figure 1: Electron microscope images of WH (a) untreated (1,500X), (b) untreated (3,000X), (c) 1% H_2SO_4 , (d) 2% H_2SO_4 , (e) 3% H_2SO_4 , (f) 4% H_2SO_4 ; all treated WH is 1,500X (pretreatment at 80°C, for 60 min).

The DSA treated WH shows more effect on the surface due to its retained moisture, and dilute acid penetrates through the substrate to disrupt the finer structure [51]. Thi *et al.* [61] reported that H_2SO_4 pretreatment of WH caused compression of the carbohydrate content with a major collapse of cellulose fibers. Therefore, pretreatment induced physical changes in biomass by removing the external fibers and increasing the surface area [62].

At the same acid concentration, increasing the temperature and reaction time, increased rough and broken surface. The optimum DSA pretreatment condition was chosen by the high cellulose content obtained from compositional analysis. Our results showed the optimum condition at 2% H_2SO_4 (80°C, 60 min). Then, SEM images were compared in various sulfuric acid concentrations at 80°C, 60 min. However, more broken surfaces indicated the higher cellulose and hemicellulose released.

3.3 FTIR analysis

The FTIR analysis was carried out to examine the

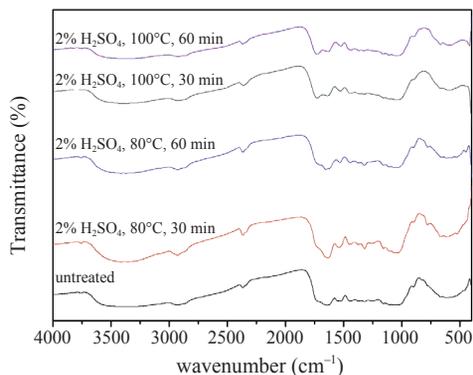


Figure 2: FTIR spectra of untreated WH and different DSA pretreatments.

changes in chemical composition and structure by comparing the FTIR spectra of WH before and after pretreatment (Figure 2). The FTIR profiles in all samples showed the similar patterns with a small changes of intensity. The intensity of FTIR spectra changing refers to the transformation in the sample composition while the broadening peak indicates the occurrence of weaker intra- and intermolecular hydrogen bonding and lower crystallinity [63].

The comparison of FTIR spectra in native WH and DSA treated WH, the intensity of peaks at 1728 cm^{-1} was slightly decreased that revealed the deformation of $\text{C}=\text{O}$ (stretching) in hemicellulose [64]. With an increase in reaction time and temperature, the peak intensities decreased which were observed in DSA treated WH samples and implied to deplete in hemicellulose content. The hemicellulose reduction was caused by deformation of hemicellulose into small molecules. The earlier reports, FTIR spectra at 1043 , 1162 , and 1720 cm^{-1} were attributed to the $\text{C}-\text{O}$, $\text{C}-\text{C}$ (stretching) or $\text{C}-\text{OH}$ (bending), $\text{C}-\text{O}-\text{C}$ vibration in hemicellulose, and carbonyl stretching of glycosidic linkage and hydroxyl groups of hemicellulose, respectively [65]–[67]. The FTIR spectra at 1441 , 1388 , 1321 , 1169 , 1056 , 1049 , and 897 cm^{-1} are associated with the cellulose [66], while spectrum around 2900 cm^{-1} is reported to $\text{C}-\text{H}$ stretching vibration band of cellulose component [68]. The FTIR spectra at 1105 cm^{-1} is typically related to crystalline cellulose [69]. The lower peak intensity indicated to less crystalline cellulose structure. Moreover, The DSA treated WH samples showed the lower intensity of FTIR spectra-related cellulose than untreated WH because of sulfuric

acid hydrolysis [70]. The FTIR spectra at 1740 cm^{-1} corresponds to both ionic and acetyl ester bonds of ferric and *p*-coumaric acids of lignin [71]. The DSA treated WH samples had similar patterns because of clearly unchanged in lignin content.

The FTIR analysis revealed the consistent results with compositional analysis (shown in Table 2) that the intensity of FTIR spectra-related hemicellulose was decreased in DSA treated WH while the hemicellulose content was reduced by solubilization during DSA pretreatment. The FTIR spectra-related lignin showed similar patterns in all WH residuals, as almost no lignin was removed from the DSA treated WH. The cellulose content in DSA treated WH was increased due to the hemicellulose removal by pretreatment. Then, the remaining cellulose fraction in DSA treated WH was higher than untreated WH.

3.4 XRD analysis

X-ray-based measurements of crystallinity index (CrI) were used for analysis the DSA treated and untreated WH samples. The crystallinity index values can be analyzed by XRD and NMR with more accurate [72]. Figure 3. shows the XRD curve of all samples. Peaks appear at $2\theta=18.0^\circ$ and 22.6° , suggesting the characteristic of amorphous and crystalline regions, respectively [48]. The CrI denotes the amount of crystalline cellulose present in the lignocellulosic biomass and its value depends on the chemical composition of biomass. The CrI of untreated WH was approximately 46% which was lower than DSA treated WH. These results occur when non-crystalline components is removed [73]. The different intensity of peaks between untreated and treated samples indicates in the different CrI [74].

The results showed that DSA pretreatment could increase the CrI of WH. The CrI in DSA treated WH samples was 48, 51, 55, and 49% when treated with 2% H_2SO_4 at $80^\circ\text{C}/30\text{ min}$, $100^\circ\text{C}/30\text{ min}$, $80^\circ\text{C}/60\text{ min}$, and $100^\circ\text{C}/60\text{ min}$, respectively. There was an increment in both crystalline and amorphous regions of cellulose when increased temperature and reaction time. These results were agreed with the previous study that the increment of crystallinity index in dilute acid pretreated materials caused by the breaking down of the amorphous cellulose region [75]. The acid pretreatment process leads to hydrolyze hemicellulose resulting in the xylose releasing and loss of hemicellulose content. Moreover,

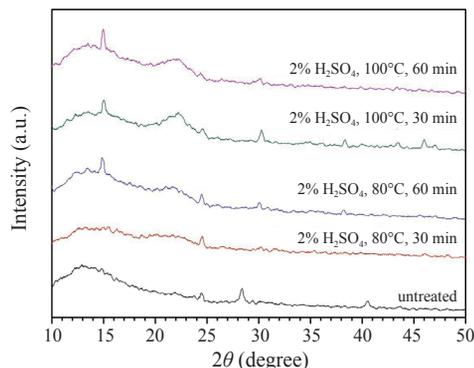


Figure 3: XRD patterns of untreated WH and different DSA pretreatments.

the dilute sulfuric acid pretreated WH at moderate temperature has been reported to be used to remove hemicellulose and recover the maximum xylose while cellulosic fraction remained in unhydrolyzed form [75].

Furthermore, thermochemical pretreatments can change the crystalline region of cellulose by disrupting inter/intra hydrogen bonding of cellulose chains [18]. The slight changes of CrI among DSA treated WH samples occurred because DSA was not effectively diffused through the entire particle. Similarly, cellulose microfibril is less effect in enzymatic accessibility due to recalcitrant structure to be immersed [40]. Contrasting to the previous report, the thermal pretreatment could reduce the cellulose crystallinity of WH [53]. Besides that, the reduction of cellulose content and CrI is owing to the complex forms breaking down into ordinary forms [75]. According to the remaining components after DSA treatments, higher cellulose and lower hemicellulose contents were owing to less solubilize cellulose than hemicellulose during acid pretreatment, while both crystalline and amorphous cellulose structures still remained in DSA treated WH residuals. The CrI of DSA treated WH depended on the amount of the crystalline region remaining in WH residual. As XRD results, the harsh pretreatment condition can disrupt the crystalline region, and loss CrI when increase the temperature (80 to 100°C) and reaction time (30 to 60 min).

4 Conclusions

This study performed the DSA pretreatment of WH at moderate temperature which is considered to be a mild

pretreatment process compared to high concentrated acid in the thermal pretreatment process. The potential advantages of this study are to reduce amount of chemical usage and waste releasing. Our strategy tests obtain the changes of structure and surface in WH samples that benefits to remove the undesired components and enhance the further hydrolysis process. The DSA pretreatment of WH was effective in uses of 2% H₂SO₄, at 80°C for 60 min. In this study, the DSA pretreatment of WH has been studied and proven to be a practicable suggestion in structural changes. Due to its fraction, it must be continued with further studies on the bioconversion of sugars, compounds releasing, and value added products. The optimum pretreatment process is promising to develop for further research, to improve efficiency, and make the process economically viable.

Acknowledgments

The authors are grateful to Biology and Chemistry departments, Mahasarakham University, for facilities and financial support.

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