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An Investigation of Cellulose, Hemicellulose and Lignin Co-Extraction from Water Hyacinth

Sharmin Sultana¹, Zakia Akter Sonia¹, Md. Mahmud¹, M. Mottakin^{1,2}, Jahid Bin Haider¹, Shoeb Ahmed³, Md. Mosaddek Hossen^{1*}

¹ Department of Applied Chemistry & Chemical Engineering, Bangabandhu Sheikh Mujibur Rahman Science and Technology University (BSMRSTU), Gopalganj, Bangladesh

² Solar Energy Research Institute, Universiti Kebangsaan Malaysia, Selangor, Malaysia

³ Department of Chemical Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh

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ABSTRACT

Water hyacinth, an abundant aqueous source of biomass, can be considered as a cash crop if properly utilized. As a lignocellulosic biomass, water hyacinth consists of three major chemical components-cellulose, hemicellulose, and lignin. These components have their direct industrial applications and can be used as raw materials to synthesize numerous chemicals. The objective of this study was to co-extract the cellulose, hemicellulose, and lignin from water hyacinth. Hemicellulose and lignin were isolated from water hyacinth by acidic and basic treatment, respectively. The operating conditions (concentration, temperature, and time) of the acid and basic treatment processes were optimized based on the hemicellulose and lignin yield. The solid residue was further oxidized by a bleaching process to obtain cellulose. The yields for cellulose, hemicellulose, and lignin-rich solids were determined as 20.5%, 7.9%, and 13.8%, respectively. The products were confirmed and characterized by FTIR and XRD. Highly crystalline nanocellulose particles were produced. From XRD, the crystallinity index and average crystallite size were calculated as 61- 67.59% and 4.26 nm, respectively.

GRAPHICAL ABSTRACT



Introduction

Fossil fuel has been used as a famous nonrenewable source to produce fuels or chemicals over the last decade, but a large amount of CO_2 is released from burning fossil fuels during the process. Concerning the global warming effect and the deficiency of fossil fuels, it is essential to obtain alternatives. Lignocellulosic biomass being abundant can be a good choice as a renewable energy source. According to the International Energy Agency (IEA), the global demand for biofuel is expected to increase massively by 2050 [1]. The uses of biomassderived fuels and chemicals can help to reduce carbon footprint. Lignocellulosic biomasses are a non-starch, non-fibrous part of the plant, and not a constituent of the human food chain. Water hyacinth is a potential candidate for the source of lignocellulosic biomass because of its rapid growth and abundance. Originating from the Amazon basin in South America, it spread to the tropical, sub-tropical warm, and rainforest region since the 1800s. Its growth rate is so high that it can double its mass in 5 days. It is considered as a weed in the aquatic system and mostly

abandoned, so utilization of water hyacinth can be advantageous and add great value to the economy. Water hyacinth belongs to the family Ponte deriaceae, related to the family Liliaceae. Water hyacinth is categorized as herbaceous plants which are seasonal and they die at the end of the growing season.

Lignocellulosic biomasses are mainly composed of three kinds of polysaccharides i.e. cellulose, hemicellulose, and aromatic polymer lignin (Figure 1a). These structural components can be used to produce various useful fuels and chemicals such as ethanol, biodiesel, glucose, xylitol, xylonic acid, furfural, levulinic acid, phenol, vanillin, etc. [2-4]. These components are also directly used in different applications such as biocomposites, dyes, packaging, medical technologies, nanomaterials, nanotechnologies, adhesives, bioplastics, etc. Therefore, the extraction of cellulose, hemicellulose, and lignin is an important step for the valorization of biomass. The average composition of the plant materials can be found at 40 - 55% of cellulose, 15 - 35% of lignin, and 25 - 40% of hemicellulose [5].

Cellulose is the most abundant chemical component in lignocellulosic biomass which is mainly composed of D-glucose linked together by β -1,4 glycosidic bond. Cellulose is mainly a longchain linear, stereoregular, and semi-crystalline polymer. The actual size of cellulose can be determined by the degree of polymerization which indicates the number of glucose units. The content of cellulose in the herbaceous plant is 30 to 40%, in woods 45 to 50%, in bast plants 60 to 70%, and in cotton fibers 90% [6]. The application of cellulose-based materials is increasing because of their being environmentally friendly and renewable sources. Cellulose nanocrystals show high mechanical

strength and surface area, biocompatibility, and biodegradability. Nanocellulose has been used in the applications of polymer nanocomposites, reinforcing packaging, biomedical agents, implants, anti-counterfeit technologies. iridescent films, greenhouse plastics, chiral nematic, particle tracking, electronic, foams, aerogels, rheological modifiers, etc. Besides, cellulose can be used to synthesize many chemicals such as levoglucosenone, y-lactone, furanose, furfural, 5-methoxymethylfurfural and their derivatives, furans, aromatic hydrocarbons, aldehydes, ketones, formic acid, acetic acid, ethanol, etc. [7, 8].



Figure 1. (a) Chemical structures of lignin, cellulose, and hemicellulose [9,10]. (Reprinted and adapted with permission from ref. [9]. Copyright (2019) Elsevier) and (b) Monomers of lignin [11]

Hemicellulose is the complexed branched hetero-polymer consisting of a mixed polymer of five and six-carbon monosaccharide molecules. Hemicellulose is consisting of a polymer of glucose, mannose, xylose, arabinose, and other five and six-carbon monosaccharides. The main amorphous polymer groups in hemicellulose are xylan, mannans, and galactans. The main characteristics that separate hemicellulose from cellulose are a lower degree of polymerization, more soluble than cellulose, and branched with a degree of polymerization of 100-200. Hemicellulose has four major classes-(a)

unbranched chains such as (1-4) linked xylans or mannans, (b) helical chains such as (1-3) linked xylans, (c) branched chains such as (1-4) linked galacto-glucomannans, and (d) pectic substances such as polyrhamno galacturonans. It has been reported that water-soluble xylans extracted from some medicinal plants have immunomodulating activities [12]. Hemicelluloses are used for the synthesis of xylitol, furfural, cationic polymers, hydrogels, ester derivatives, and thermoplastics [13]. They have applications food, packaging, in biomedicine, textile, cosmetic, pharmaceutical, and papermaking industries. Hemicellulose can also be used as stabilizers, film formers, emulsifiers, decorative paints, adhesives, paper coatings, thickeners, latex, xylooligosaccharides, high-density fuels, and hemicellulose-reinforced nanocellulose hydrogels [14].

Lignin is an aromatic biopolymer and a binding agent for cellulose and hemicellulose to hold them together. It also helps to transport water and nutrients to plant cells, protect from pathogens, and provide structural rigidity. Lignin is made of three monomers i.e. coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol (Figure 1b), and thereby consists of three phenyl propanoid skeletons i.e. syringyl (S), guaiacyl (G), and p-hydroxy phenyl (H). The ratio of these units differs in plants depending on the species, growing environment, location, age, and extraction method. According to dry weight, hardwood contains about 18 to 25% lignin and softwood contains 25 to 35% lignin. It is highly insoluble in water, and even not soluble in sulfuric acid. Lignin provides the compressional strength to the plant cell wall whereas cellulose provides the flexible strength to the plant. Lignin with a higher phenolic content can be utilized industrially to produce phenol-formaldehyde resins. Lignin has applications in the area of dispersal agents, emulsifiers, dyes, lubricants, floorings, binding. synthetic biofuels, sequestering paints, bioplastics, thermosets, nanocomposites, nanoparticles, and fuels to treatments for roadways [15].

Numerous researches have been conducted for the extraction of cellulose, hemicellulose, and lignin individually from different biomass sources. Several physical pretreatment techniques such as mechanical (milling, grinding, extrusion), irradiation (gamma rays, electron beams, and microwaves), gas explosion, chemical pretreatment techniques such as alkaline, acid hydrolysis, Enzymatic hydrolysis, ozonolysis, organosolv, ionic liquid pretreatments, etc. have been employed ever since [16,17]. There are several techniques for determining each of the structural components such as TAPPI T222 [18], NREL LAP [19], DE method [6], Kurschner and Hoffer [20], APPITA method P11s-78 [21], etc., but these techniques do not always describe the co-extraction of all the desired components. Several efforts have been accomplished in the co-extraction or fractionation of these components from different biomass sources using different techniques and chemicals [22-25].

In this work, the co-extraction of cellulose, hemicellulose, and lignin from the stem of water hyacinth was performed by a chemical method combining three main steps i.e. acidic, basic, and bleaching processes carried out stepwise to extract hemicellulose, lignin, and cellulose, respectively. Common laboratory chemicals i.e. sulfuric acid, sodium hydroxide, sodium chlorite, acetone, etc. were used in our work. The optimum conditions of the first two steps were determined based on the amount of the respective products. Finally, the manufacturing processes as shown in Figure 2 were applied to identify the yield of each product. The products characterization was performed using FTIR and XRD. XRD was used to identify the cellulose crystallinity.

Materials and methods

Chemicals and Raw Materials

Water hyacinth (*Eichhornia crassipes*) was collected from the pond in the neighboring area of BSMRSTU in Gopalganj. Stems of water hyacinth samples were cut into small pieces (1 cm). The stem samples were blended into a paste and then dried in an oven at 80 °C for 12 h as shown in Figure S1. The dried samples were ground to powder form and passed through a wire mesh screen (600 μ m). The fine powder samples were stored in a sealed plastic bag and then kept in a desiccator to avoid moisture absorption. Hydrochloric acid, sodium hydroxide

pellets, sulfuric acid, and acetone were purchased from Merck KGAa, Germany.

Treatment Optimization

Acidic treatment

3 g of dried water hyacinth sample was added in 50 mL acid (H₂SO₄) solution in a 500 mL flat bottom flask. The reaction flask was set on an electric hot plate and a condenser was attached to the flask (Figure S3a). After the solution reached the selected temperature, the acidic treatment reaction was started by adding the water hyacinth sample. The treatment was performed at different temperatures (70-110 °C), concentrations of H_2SO_4 (0.5-10% v/v), and reaction time (30-120 min). The optimum reaction conditions were determined based on the yield of hemicellulose-rich solid. After cooling, the supernatant liquid was separated from the solid residue by filtration. The solid residue (R-1) was washed properly with water, and then oven-dried at 80 °C for 2 hr. The products and intermediates are shown in Figure S3.

Basic treatment

To obtain the optimum reaction conditions, 2.5 g of water hyacinth sample was added into NaOH solution in a three-necked round bottom flask. The flask was kept on an electric heating mantle and a condenser was attached to the top Figure S4b. The treatment process was operated at different temperatures (70-102 °C), time (45-180 min), and concentrations of NaOH (7-17.5 % w/v).

The optimum conditions were obtained based on the amount of lignin-rich solid produced. The acid-treated solid (**R-1**) was later treated in NaOH solution at the observed optimum conditions to separate lignin from the solid content and the yield percentage was calculated thereby. The treated solution was filtered by Whatman filter paper and the solid residue was collected and dried in an oven dryer. The products and intermediates are shown in Figure S4.

Co-extraction process

The proposed co-extraction process consisted of acidic, basic, and bleaching steps. A part of the extractives i.e. waxes, pectin, etc., and also hemicellulose were expected to be removed during the acidic treatment at hot conditions. Since hemicellulose gets precipitated in ethanol/ acetone solution, the dissolved hemicelluloses were separated from the acid-treated solution by the addition of acetone, and then the acid-treated solid sample (R-1) was treated with a basic solution to extract lignin. The dissolved lignin was precipitated by lowering the pH of the basic treated solution to 5.0. The bleaching process using NaClO₂ was applied to remove the remaining lignin present in the cellulose-rich solids.

Acidic treatment

5g of the raw sample (stem of water hyacinth) was added in a flat bottom flask containing 100 ml solution of 6% (v/v) H₂SO₄. The flask which was attached with a condenser was placed on a hot-plate magnetic stirrer. The acidic treatment was conducted for 45 min at the optimized temperature of 96 °C. The liquid was kept stirred using a magnetic stirrer bar at 80 rpm. The solid residue after the treatment was separated from the acid-treated solution by filtration using Whatman filter paper. The solid residue was washed several times with water and dried in an oven for 2 hr at 80 °C. The acid-treated solid residue (R-1) was weighed 3.654 g.

Hemicellulose extraction

40 mL acetone was added into 100 mL of acidtreated liquid solution and the solution was kept at vibration for 2 hr at 130 rpm in an orbital shaker. The solution was then kept steady for 12 hr and centrifuged at 800 rpm for 20 min. Hemicellulose was precipitated in the test tube. The supernatant liquid was poured off and water was then added to the solid which was later centrifuged for 5 min. The supernatant liquid was again poured off from the top. The collected solid went through bleached by reacting in a solution of 1.3 % (w/v) sodium chlorite for 2 hr at 80 °C. The bleached solid was washed with water and dried in an oven at 60 °C for 1 hr. The product is denoted by P-2.



Figure 2. Process block diagram for the co-extraction of cellulose, hemicellulose, and lignin.

Basic treatment and lignin extraction

3.654 g of the residue R-1 was base-treated with 100 mL of 15.1 % (w/v) NaOH for 90 min at 102 °C at the same experimental setup used for acidic treatment. Similarly, the liquid portion after the basic treatment was separated from the solid residue by filtration.

The pH of the solution was reduced to 5.0 by adding HCl and the lignin started to precipitate from the solution. The solution was kept steady for 12 hr and the top transparent layer was poured off carefully, and then the bottom portion of the liquid containing the suspension of solid particles was centrifuged for 20 min at 800 rpm. The solid component was precipitated at the bottom of the test tube. After separating the liquid, the precipitated solid was collected. The salt that was produced from the neutralization reaction was present in the solid.

Therefore, the collected solid was washed 2-3 times with water to dissolve and remove the salt present in it. After that, the solid product (P-3) was oven-dried at 60 $^{\circ}$ C for several hours.

Bleaching process and cellulose extraction

The solid residue (**R-2**) from the basic treatment process was washed with hot water several times and dried in an oven at 80 °C. The sample was further bleached with 1.7 % (w/v) NaClO₂ at 80 °C for 4 hr. The solid residue (**P-1**) was separated from the solution by filtration and dried. The products and intermediates are shown in Figure S5.

FTIR Analysis

The functional group components present in different samples were identified using FTIR analysis by an FTIR spectrophotometer (IRPrestige- 21, Shimadzu, Kyoto, Japan).

The powdered product samples (P-1, P-2, and P-3) were placed over potassium bromide pellets, and the infrared spectrums were recorded from the range of 4000 to 400 cm⁻¹. The attenuated total reflection Fourier transform infrared (ATR-FTIR) was used to analyze the chemical changes of the samples before and after acidic and basic treatment. ATR-FTIR spectral analysis was performed within the range of 4000 to 700 cm⁻¹.

X-ray diffraction (XRD) analysis

The X-ray diffraction method was used to determine the degree of crystallinity of the extracted cellulose. The XRD patterns were obtained with an X-ray diffractometer (Rigaku Ultima-IV) at room temperature. For analysis, the sample (P-1) was ground into a fine powder using a blending mill and then pressed into a sample holder. The intensity of the reflection was measured using a monochromatic Cu-K α radiation source (λ = 0.15406 nm) over the range of 10° ≤ 20 ≤ 70° at a scan speed of 3°/min. The working lamp parameters were set as follows: υ = 40 kv, I = 40mA, receiving slit =0.3 mm.

The crystallinity index (Ic) of the cellulose was calculated using the Segal method [26-28],

$$I_c = \frac{I_{200} - I_{am}}{I_{200}} \times 100\%$$
 (1)

Where, I_{200} is the peak intensity of crystalline material at $2\theta = 22.33^{\circ}$ and I_{am} is the intensity minimum of the amorphous material between 200 and 110 planes (I_{am} , $2\theta = 15.78^{\circ}$)

The crystallinity index can also be calculated as the following equation.

$$\frac{\text{The crystallinity index }}{\text{Area of all crystalline peaks}} \quad (I_c) = \\ \times 100\%$$

The crystallite size (CS) of P-1 was calculated by Equation (3) [29,30]:

$$CS = \frac{K\lambda}{\beta\cos\theta} \tag{3}$$

Where, K = 0.89 (Scherrer's constant), β = FWHM (full-width at half-maximum), and λ = wavelength of the X-ray.

Results and Discussion

Optimum conditions for the basic treatment process

The effects of H₂SO₄ concentration, time, and temperature on the acidic treatment were analyzed. Hydrogen bonds between hemicellulose and cellulose are broken in the presence of acid [31]. Therefore, the mass of solid residue is expected to decrease after the acidic treatment because of the removal of hemicellulose, pectin, and others. Different concentrations of acid were applied at a constant temperature (96 °C) and time (45 min) to understand the effect and it was observed from Figure 3a that the mass of residual solid was decreasing with the increase of concentration of H₂SO₄, although the amount of the production of hemicellulose-rich solid (P-2) reached a peak and then it decreased. The data thus indicates that the increase of acid concentration helps to remove the acid-soluble components, but either the acid-hydrolyzed hemicellulose components were depleted or the produced hemicelluloses were converted into other soluble compounds above a certain concentration. From the observation, the optimum acid concentration was determined to be 6 % (v/v).

Similarly, the effect of reaction time was varied at a definite temperature (96 °C) and concentration (6%(v/v) H₂SO₄). After a certain time (45 min) as shown in Figure 3b, the mass of residue reached a plateau that indicates that the disintegration of acid-hydrolyzed hemicellulose and other components was completed in 45 min. The amount of produced hemicellulose, on the other side, showed an increase up to 150 mg at 45 min and then a drop of 97 mg of hemicellulose was noticed in the next 8 min. The mass of hemicellulose-rich solid (P-2) reached a steady value thereafter. The data indicates that the disintegrated hemicelluloses were converted to other chemicals or water-soluble compounds at the reaction conditions. After 45 min, the rate of disintegration of hemicellulose from the water hyacinth sample was getting lower than the conversion of hemicellulose into other forms. The data resembles the previous study where it was proposed that long extraction time may induce the change of polysaccharides molecule structure [32]. Therefore, the optimum time for acid treatment was considered as 45 min.



Figure 3. Effect of reaction conditions (a) concentration of H₂SO₄, (b) time, and (c) temperature on the acidic treatment.

The effect of temperature on the acid treatment was also studied at constant time (45 min) and concentration of 6 % (v/v) H_2SO_4 , as demonstrated in Figure 3c. A typical relation was established where a peak point for the produced mass of hemicellulose-rich solid (P-2) was observed at 96 °C.

From these optimization experiments, the reaction conditions for the acid treatment were determined as 96 °C, 45 min, and 6 % (v/v) H_2SO_4 .

Optimum conditions for the basic treatment process

The effect of the reaction conditions for basic treatment was experimentally studied to determine the optimum conditions based on the amount of the produced lignin-rich solid (Figure 4).

The effect of NaOH concentration is an important factor that influences the extraction efficiency of lignin. It was very clear that at

constant temperature (102 °C) and time (60 min), with the increase of NaOH concentration the disintegration of lignin was increasing up to a limit. The lowest amount of mass of residue and the highest amount of lignin-rich solid were produced at 15.1 % (w/v) NaOH and thereby this concentration was determined as the optimum. Similarly, at constant temperature (102 °C), and concentration (15. % (w/v) NaOH), the optimum time for the basic treatment operation was found at 90 min. At the constant time (90 min) and concentration (15. % (w/v) NaOH), an unusual effect of temperature on the production of lignin-

rich solid was observed. Although the lowest amount of residue was observed at 90 °C, the mass of produced lignin was increasing exponentially with the increase of temperature. Therefore, the optimum temperature can be either 90, or 102 °C based on the lowest mass of residue, or the highest mass of produced ligninrich solid respectively. A temperature higher than 102 °C was not used since this was getting closer to the boiling point of the solution. Concerning each aspect, the optimum conditions were selected as 102 °C, 90 min, and 15.1 % (w/v) NaOH for the basic treatment.



Figure 4. Effect of reaction conditions (a) concentration of NaOH, (b) time, and (c) temperature on the basic treatment.

Yield %

The optimum conditions determined above were applied to the co-extraction process. 1.024±0.006 g of cellulose-rich solid, 0.399 ± 0.002 g of hemicellulose-rich solid, 0.69 ± 0.09 g of lignin-rich solid was extracted from 5 g of water hyacinth sample. Thereby, the yields were determined as 20.5%, 7.9%, and

13.8% for cellulose, hemicellulose, and ligninrich solids, respectively.

FTIR analysis

Raw water hyacinth

From the FTIR-ATR graph, as shown in Figure 5a, the peaks around 3375.97 cm^{-1} indicate –OH stretching and –CH₂ stretching and thereby confirm the presence of cellulose. A broad peak at 1022.27 cm⁻¹ is typically related to the structure of cellulose and hemicellulose. The peaks observed at 1636.03 and 1411 cm⁻¹ were indicative of the presence of lignin. Besides, peaks at 2347.36, 1312.77 cm⁻¹, etc. on the graphs indicate various impurities, pectin, carboxylic acid salt, amine, or organic phosphate.

Acid-treated solid residue (R-1)

From Figure 5a, the peaks around 3915.49, 3603.02, 3377.35, 3032.09, and 2762.06 cm⁻¹ indicate the peak of cellulose because of –OH stretching and C-H stretching. The main difference between the untreated and acid-treated samples is that there is no peak at 1200-1000 cm⁻¹ which are the characteristic peaks for hemicellulose. Therefore, it is clear that the maximum amount of hemicellulose was dissolved in acid. The peak at 1687.71 cm⁻¹ indicates the conjugated ketone groups which confirms the presence of lignin.

Basic treated solid residue (R-2)

After the basic treatment, peaks around 3935.49, 3631.77, 3321.42, and 2885.50 cm⁻¹ confirm –OH and C-H stretching and thereby the presence of cellulose, as shown in Figure 5a.

Nonetheless, since the peaks appeared at 1664.13 and 1031.91 cm⁻¹, it can be concluded that small quantities of lignin and hemicellulose were still present in the basic treated sample.

Cellulose-rich Solid (P-1)

From Figure 5b, the absorbance band at 3439.08 cm⁻¹ shows a medium, broad peak which indicates the OH-stretching vibration of the OH group as well as intramolecular and intermolecular hydrogen bonds [5]. A weak, narrow peak at 2914.44 cm⁻¹ indicates the C-H stretching vibration (peak region 2900-2880 cm-¹) [33]. The absorbance at 1629.85 cm⁻¹ indicates the O-H bending of the absorbed water molecules [27]. Two weak and narrow peaks at 1371.39 and 1433.11 cm⁻¹ indicate C-O, or C-H symmetric bending vibration in polysaccharide aromatic rings [35] and C-H asymmetric bending vibration, respectively. The peak at around 1430 and 1420 cm⁻¹ correspond to the scissoring motion of cellulose I and cellulose II, respectively [36]. The band at 894.97 cm⁻¹ indicates C-H out plane bending vibration of β -glycosidic linkages between sugar units [37]. We therefore suggest the sample as the cellulose form of carbohydrate by the presence of these peaks 894.97, and 1433.11 cm⁻¹ which are associated with C-H bending vibration due to -CH₂ group, C-H asymmetric bending vibration, respectively [38]. However, there is a medium, sharp peak at 1062.78 cm⁻¹ which indicates the C-O and C-H stretching vibration and specifies the presence of typical xylan [39]. Therefore, the purity of cellulose cannot be confirmed although the XRD result confirmed the presence of crystalline cellulose-Ia.



Figure 5. (a) ATR-FTIR spectrum of raw water hyacinth, acid-treated solid residue (R-1) and basic treated solid residue (R-2) samples and (b) FTIR spectrum of product P-1as cellulose-rich solid, product P-2 as hemicellulose-rich solid, product P-3 as lignin-rich solid prepared from the stem of water hyacinth.

Hemicellulose-rich Solid (P-2)

According to Figure 5b, the FTIR spectrum of P-2 extracted from water hyacinth shows a weak, narrow band at 3406.29 cm⁻¹ indicating that internally bonded –OH stretching vibration. The absorption band at 1200 to 800 cm⁻¹ indicates polysaccharides [40]. The peaks at 1610-1639 cm⁻¹ indicate the O-H bending of the absorbed water molecules. There is a sharp, medium band at 1124.50 cm⁻¹ which indicates C-O stretching vibration and indicates typical xylan. The suitable region for xylose in the FTIR spectrum is 1125-1000 [42].

Lignin-rich Solid (P-3)

The typical functional groups present in the aromatic region of lignin are hydroxyl groups in phenolic and aliphatic structures, methyl (-CH₃), methylene (=CH₂, CH₂-), methoxy (-OCH₃) groups, and aldehydes, etc. [43,44]. The FTIR spectrum of product **P-3**, as shown in Figure 5b

shows a broad, medium peak at 3427.51 cm⁻¹ indicating the H-bonded OH stretching. There is also a sharp, weak peak which can indicate an OH stretching vibration. The absorbance band at 2922.16 cm⁻¹ shows a sharp, weak peak which indicates the C-H asymmetric stretching vibration due to the -CH₂ group. The absorption band at 1718.58 cm⁻¹ contains a sharp, weak peak which may be the -COOH or -C=O group. The absorbance at 1624.06 and 1438.90 cm⁻¹ indicated C=O stretching of the conjugated ketone group and asymmetric C-H vibration due to the deformation of the -CH₃ group in lignin, respectively. According to Kumar et al., FTIR peaks of lignin correspond to 1718.58, 1624.06, and 1438.90 cm⁻¹ [45]. Therefore, lignin can be confirmed in product P-3.

XRD

The produced cellulose-rich solid (P-1) was characterized by XRD to find the crystallinity behavior. Crystalline cellulose enhances polymer reinforcements by improving the strength and stiffness of the composites [27]. From Figure 6, the XRD spectrum of P-1 showed peaks at $2\theta = 15.78$, 22.33, and 34.6°. The peaks resemble the diffraction pattern of cellulose-I α which generally shows peaks around $2\theta = 16$, 22.6, and

 35° [46]. From the comparison, the presence of semi-crystalline cellulose-I α is confirmed in the P-1 sample. The crystallinity index was calculated as 61-67.59%, whereas average crystallite size was determined as 4.26 nm.



Figure 6. XRD spectrum of product P-1.

Limitations and Suggestions

The proposed process successfully produces cellulose, hemicellulose, and lignin from water hyacinth. However, the removal of extractives from water hyacinth at the initial stage could ensure higher yield and purity of the products. The reaction conditions of the bleaching process should be optimized in future studies. The yield of hemicellulose was very low because of it was produced from the acid-treated step only. Since hemicellulose is dissolved in a basic solution, therefore the basic treatment is expected to extract a good amount of hemicellulose. The isolation process of hemicellulose should be applied in the basic treated liquor as well to enhance the yield of hemicellulose. The purity of the cellulose product could have been improved by the modified bleaching process.

Conclusion

An optimized chemical method for the coextraction of cellulose, hemicellulose, and ligninrich solids from the stem of water hyacinth was developed in this work. The process includes acidic, basic, and bleaching processes. The optimum conditions were determined as 96 °C, 45 min, 6 % (v/v) H_2SO_4 for the acidic treatment and 102 °C, 90 min, and 15.1 % (w/v) NaOH for the basic treatment. The co-extraction process at the optimum conditions showed yields of 20.5%, 7.9%, and 13.8% for cellulose, hemicellulose, and lignin-rich solids, respectively. FTIR confirmed the corresponding functional groups for cellulose, hemicellulose, and lignin in the respective products. From XRD, the crystallinity index and average crystallite size of the produced cellulose were calculated as 61- 67.59% and 4.26 nm. Future endeavors may include the optimization of the bleaching process conditions, combining different approaches, finding purity of the components at each stage, reducing the polysaccharides conversion during the treatments, etc. The developed method is expected to be applicable to co-extract the compounds from other biomasses as well.

Data availability

The datasets generated during the current study are shown in the supplementary information.

Conflict of interest

The authors declare that there is no conflict of interest.

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Orcid

Md. Mahmud :: 0000-0002-1487-2876 M. Mottakin :: 0000-0002-4805-605X Jahid Bin Haider :: 0000-0001-6446-2202 Shoeb Ahmed :: 0000-0001-8215-5169 Md. Mosaddek Hossen :: 0000-0002-9350-0922

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