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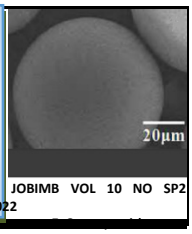

Precipitation of Xylan from Agricultural Waste Using Acid and Alcohol to Produce Bio-Polymer Film

Thivagaran Veeraiya[1], Shuhaida Harun[1]* and Mastura Abd Manaf[1]

[1]Department of Chemical and Process Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, Bangi, 43000 Kajang, Selangor, Malaysia.

*Corresponding author:
Assoc. Prof. Ir. Dr. Shuhaida Harun,
Department of Chemical and Process Engineering
Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia
Bangi, 43000 Kajang,
Selangor, Malaysia.
Email: harun.shuhaida@ukm.edu.my

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ABSTRACT

Xylan from natural sources such as agricultural waste can be used to produce biopolymer packaging films and reduce the use up of petrochemical film. In this study, three different agricultural wastes (oil palm frond, sugarcane bagasse and corn stover) were used to extract xylan by using various alkaline and acidic solvents. From the analysis of the composition of oil palm fronds, it was found that oil palm frond contains (%) 30.8 ± 0.4 glucan, 19.3 ± 0.3 xylan and 18.4± 0.8 lignin. The percentage of extraction of xylan with sodium hydroxide is higher than sulfuric acid and dimethyl sulfoxide. Xylan extracted with dimethyl sulfoxide contains acetyl qualifiers and is suitable for producing carboxymethyl xylan. For xylan deposition, the use of a high concentration of ethanol gave a high xylan precipitation. Finally, the film with sorbitol as a plasticizing material showed low water absorption and high tensile strength of 4,855 $gs^{-1}m^{-1}$ Pa and 26 Mpa respectively.

INTRODUCTION

Agriculture is a major economic factor in Malaysia. The kenaf and palm oil industries are among the important industries in agriculture. One challenge facing the industry is the waste generated from crops. Poor management of agricultural waste can cause adverse effects on the environment such as soil pollution, climate change and ecosystem disturbance. The biomass produced by the agricultural industry is rich in nutrients and carbohydrate sugars [1]. This proves that biomass from the agricultural industry has the potential to produce valuable and environmentally friendly chemicals. Kenaf stem and oil palm fronds are among the remains produced from kenaf and palm oil. Both kenaf stem and oil palm fronds contain hemicellulose which can be used to produce high value products. Hemicellulose is the second largest polysaccharide found in the world besides cellulose. 40% of the cell wall mass consists of hemicellulose and xylan is the dominant hemicellulose in the secondary cell wall [2]. Xylan has been used in various applications such as in food industry, bio-chemicals industry, renewable biofuels and the livestock industry. Xylan also suitable to apply in biopolymer packaging films [3]. Most of plastic material produced is based on petrochemical materials [4]. Petrochemical plastics have the potential to pollute the environment due to their unbiodegradable nature. The replacement of petrochemical films with biopolymer films will protect the environment [5-6].

However, the use of xylan in the industry is not well received due to the high cost and complexity in extraction and precipitation processes. Various studies have been carried out to determine the optimum conditions for precipitation of xylan from biomass. Precipitation of xylan can be carried out with alkaline solutions such as sodium hydroxide and potassium hydroxide. Ethanol is also used as an anti-solvent for the precipitation of xylan [7-10]. The purpose of this study was to determine the recovered xylan percentage in extraction of various agricultural waste and solvent. Besides that, the study aimed to determine high purity xylan with different acid solvents and optimal concentration of ethanol to precipitate high yield of xylan.

MATERIALS AND METHODS

Materials

Oil palm fronds were collected from oil palm plantation in Universiti Kebangsaan Malaysia. The chemicals used in this experiment were ethanol, acetic acid, nitric acid, sodium hydroxide, hydrochloric acid, ethanol, 2-propanol, sodium monocloroacetate, glycerol and sorbitol.

Biomass Preparation

Oil palm fronds were cut about average length of 1 to 3 m long. The juice from the oil palm fronds was removed by pressing through a sugarcane presser machine model SCM (6.5 hp petrol-driven, Zheijiang Sheng, China) and was dried for 72 hours. Then, the sample was ground to particle sizes about 2mm using a grinding machine (Fritsch, Idar-Oberstein, Germany). Subsequently, the sample was sieved using a 0.5 mm mesh to remove powdered particles. The samples were sealed and stored at 4 °C [1].

Chemical Composition Analysis

The chemical composition analysis of oil palm fronds was carried out based on methods developed by the National Renewable Energy Laboratory (NREL) including the identification of carbohydrates, lignin and ash [11]. Water extraction was carried out of palm oil, followed by ethanol extraction using ASE 350 (ASE-Dionex, Sunnyvale, CA, USA) to remove extractive components. 0.3 g of biomass was extracted with 3 mL 72% sulfuric acid at 30 °C for 60 minutes, followed by dilution with 84 mL of distilled water [1].

Xylan Extraction

The extraction of xylan has been studied using different solutions and conditions as shown in **Table 1**. The xylan extraction was initially investigated by varying the solvent concentration, temperature, time and solid to liquid load. During the extraction, black liquor was generated after treating the biomass.

Table 1. Xylan extraction method from various biomass.

Biomass	Study	Solvent	Conc. (%)	Temp (°C)	Time (min)	Solid load (%)	Reference
Oil palm fronds	1	NaOH	6	100	60	10	[1]
	2	H_2SO_4	1.5	121	45	10	[14]
	3	HNO_3	4	130	20	12.5	[15]
Sugar cane bagasse	4	NaOH	1.75	75	25	10	[16]
	5	H_2SO_4	2	122	24	10	[17]
	6	C_2H_6OS	38	24	1440	5	[18]
Corn stover	7	NaOH	10	75	120	5	[19]
	8	H_2SO4	2.13	121	180	10	[20]
	9	C_2H_6OS	38	70	1440	7	[21]

Xylan Precipitation

Black liquid undergoes 2-step precipitation using hydrochloric acid and ethanol. The identified black liquid was centrifuged at 10000 rpm for 15 minutes. Precipitation products known as lignin are filtered and dried with a freezer (Martin Christ Alpha 1-4 LSC freeze dryer). The supernatant from lignin precipitation was studied using ethanol (20, 40, 60 and 80%). The mixture was stirred at 10000 rpm for 15 minutes. The precipitate is known as xylan. Xylan was dried with a freezer. Xylan recovery and yield were measured using Eq. 1 and 2 respectively.

$$\text{Xylan recovery}(\%) = \frac{\text{Xylan yield}(\%)}{\text{Xylan in raw biomass}\ (\%)} \text{x}100 \quad (1)$$

$$\text{Xylan yield} = \frac{\text{Dry weight of recoverd xylan (g)}}{\text{Dry weight of biomass sample (g)}} \times 100 \quad (2)$$

Sugar Composition of Extracted Xylan

Hydrolysis of lignin and xylan precipitate was carried out with sulfuric acid to determine the composition of sugar. Sugar composition was determined using HPLC (UltiMate 3000 LC RefractoMax 520, ERC, Buchholz, Germany) at 40 °C [1].

Fourier Transient Infrared Analysis (FTIR)

FTIR analysis was performed on biomass, xylan and commercial xylan with FTIR spectrometers (Thermo Fisher Scientific, MA, USA) at frequencies of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} to identify functional groups [1].

Bio-Polymer Film Production

10 g of xylan was dissolved in 50 ml of 25% sodium hydroxide solution at 30 °C. 70 ml 2-propanol was added to the mixture and stirred for 30 minutes. 8.78 g sodium monochloroacetate was added and the temperature was raised to 65 °C. The mixture was left for 70 minutes and neutralized with acetic acid (2M). The resulting carboxymethyl xylan was precipitated with ethanol. 2 g of plasticizer (Glycerol, sorbitol and glycerol/sorbitol) were added as a plasticizer and stirred for 5 minutes. The mixture was homogenized with homogenizer (Ultra-Turrax T25 homogenizer IKA brand) at 7600 rpm for 2 minutes, then 12,000 rpm for 2 minutes. The resulting mixture was poured into a Petri dish and dried at 30 °C.

Mechanical Properties of Bio-Polymer Films

The mechanical properties of the packing film were measured using a tension test machine (Thwing-Albert Instrument Co.), at 22 °C and a relative humidity of 50%. The resulting film is cut into small samples of 80 mm and 15 mm wide. The tests were conducted at 10 mm min^{-1} and 50mm distance.

Water Vapor Permeability

Water vapor permeability was measured by gravimetric method using Regmed-PVA / 4 tools. Each film was placed in an aluminium box with calcium chloride to ensure 0% relative humidity. The film was coated with paraffin and kept at 22 °C with a relative humidity of 50%. Sample mass was measured every 2 hours for 48 hours. The mass graph against the plotted time and the water vapor transmission rate are calculated by the ratio of the gradient of the graph to the surface area of the film. Water vapor solubility is calculated based on the following formula [22]:

$$WVP = \frac{WVTR}{\Delta P} = \frac{WVTR}{P(R1-R2)}\ x\ 100 \quad (3)$$

RESULTS AND DISCUSSION

Composition of Oil Palm Frond

Potential of an agricultural waste as a feedstock can be initially identified by its components composition and compared with another biomass. **Table 2** shows the data on the composition of palm fronds from this study and the comparison with other studies. From this study, it was found that the oil palm frond consists of 30.8 ± 0.4% glucan, 19.3 ± 0.3% xylan and 18.4 ± 0.8 % lignin. The amount of carbohydrates found in palm oil fronds was 50.1 ± 0.7%. The total amount of carbohydrates found in this trial was lower than in other trials. This difference is due to several factors in the selection of palm oil fronds. The maturity of oil palms, oil palm fronds, weather conditions, and the type of palm trees are among the factors that affect the composition of oil palm fronds.

Table 2. Composition of oil palm frond.

Component	Present study	Ref [23]	Ref [24]	Ref [25]	Ref [26]
Glucan	30.8 ± 0.4	34.7 ± 4.2	41.7 ± 0.5	46.4 ± 2.2	47.3 ± 0.9
Xylan	19.3 ± 0.3	19.4 ± 3.8	18.5 ± 0.2	15.3 ± 0.9	18.2 ± 0.6
Arabinan	N. D.	N. D.	1.2 ± 0.3	N. D.	N. D.
Total lignin	18.4 ± 0.8	20.7 ± 0.5	20.5 ± 0.4	23.5 ± 3.6	23.9 ±1.2
AIL	16.3 ± 0.3	19.6 ± 0.2	N. D.	18.2 ± 3.6	N. D.
ACL	2.1 ± 0.5	1.1 ± 0.3	N. D.	5.3 ± 0.5	N. D.
Ash	0.44 ± 0.3	1.1 ± 0.1	4.2 ± 0.4	1.43 ± 0.1	3.1 ± 0.9

*N.D., No Data. AIL, Acid Insoluble Lignin and ACL, Acid Soluble Lignin

Xylan Extraction

Various methods were implemented with different biomass, solvents, and conditions to determine the highest percentage of xylan extraction. **Fig. 1** shows the results of xylan extraction from Study 1 to 9. The result shown that sodium hydroxide was more effective than sulfuric acid. This is because extraction with sodium hydroxide causes a saponification reaction. The saponification reaction reduces the degree of polymerization, increases the surface area and breaks the bond between lignin and carbohydrate [27]. Although extraction with dimethyl sulfide gives a low extraction percentage it will prevent deacetylation. Acetyl group is essential to produce carboxylmethyl xylan.

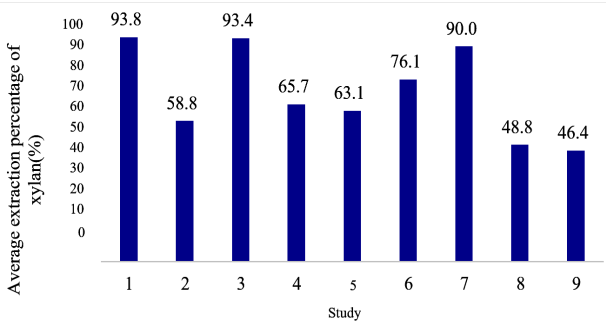

Fig. 1. Xylan extraction yield (%) of Study 1 to 9.

Structure of Extracted Xylan

The structure of xylan discussed in this section is based on the studies in **Table 2**. Xylan from different sources has a different structure. The use of different solvents also affects the structure of xylan [28]. The structure of xylan is very important as it will affect the application of the xylan. **Table 3** shows the results of the FTIR analysis from Study 1, 6 and 9.

Table 3. Groups of functions found on xylan extracted from different biomass and solvents.

Biomass	Solvent	The functional set contained in the xylan	Reference
Oil Palm fronds	NaOH	C-C, C-O, C-OH, C=O	[13]
Sugarcane bagasse	C_2H_6OS	C-C, C-O, C-OH, C=O, C_2H_3O	[18]
Corn straw	C_2H_6OS	C-C, C-O, C-OH, C=O, C_2H_3O	[21]

Composition of Black Liquor

Extraction of xylan by treating the biomass with solvent was resulted black liquor. **Table 4** and **Fig. 2** show the black liquor composition of different biomass and solvent. Significant differences can be seen between the composition of the oil palm frond and the corn stover. Oil palm frond contained high glucan (28.45 %) compared to sugarcane bagasse (3.0 %) and corn stover (2.13 %). Besides that, acetic acid and furfural were not presented in the oil palm fronds black liquor. The contents of foreign materials such as acetic acid, furfural, fructose, galactose and arabinan are higher in corn stover than palm oil frond. The presence of the foreign materials will affect the precipitation and purity of the xylan.

Table 4. Composition of black liquor of different biomass.

Biomass	Solvent	Glucan	Xylan	Acetic acid	Furfural	Others	References
Oil palm frond	Sulfuric Acid	28.45	30.97	-	-	40.63	[14]
Sugarcane Bagasse	Sulfuric Acid	3.00	21.60	3.65	0.52	71.23	[17]
Corn stover	Sulfuric Acid	2.13	9.09	1.48	0.56	86.74	[20]

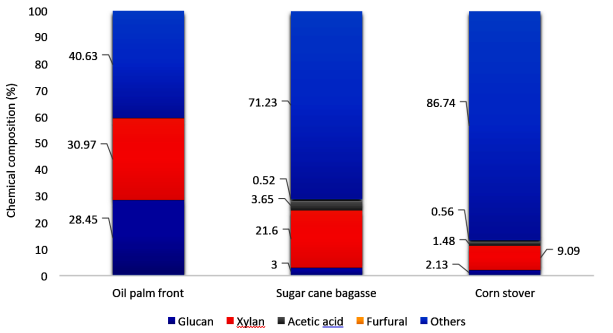

Fig. 2. Black liquor composition of different biomass.

Xylan precipitation

Xylan precipitation was carried out in two stages, named acidic precipitation, and alcoholic precipitation. The purpose of acidic precipitation is to get rid of non-xylan materials such as lignin so that pure xylan can be precipitated in alcoholic precipitation [29].

Different acid: sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, acetic acid and formic acid, were used in this process. Xylan purity was determined upon each acid precipitation. **Fig. 3** shows the purity of extracted xylan after acidic precipitation. Nitric acid resulted 88 % xylan purity compared to hydrochloric acid (83 %), acetic acid (81 %), formic acid (75 %), phosphoric acid (60 %) and sulfuric acid (52%).

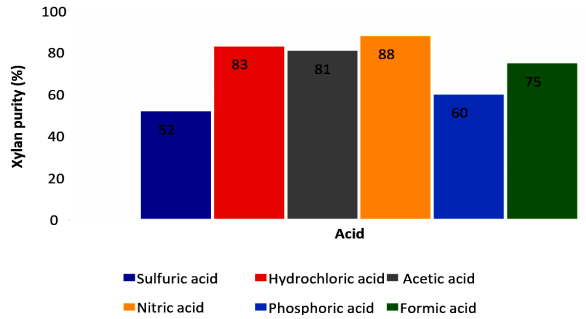

Fig. 3. Purity of xylan produced after acidic precipitation of different acids and subsequently the effect of ethanol concentration on precipitation of xylan.

The two stages of precipitation defined the different molecular weight of components. Lignin with higher molecular weight was usually obtained from the first precipitation using acid, while the hemicellulose with lower molecular weight was obtained from the second stage of precipitation using ethanol [1]. **Fig. 4** show the effect of ethanol concentration on xylan precipitation. Higher ethanol concentration precipitated more xylan, as the concentration of ethanol increased from 40 to 80 %.

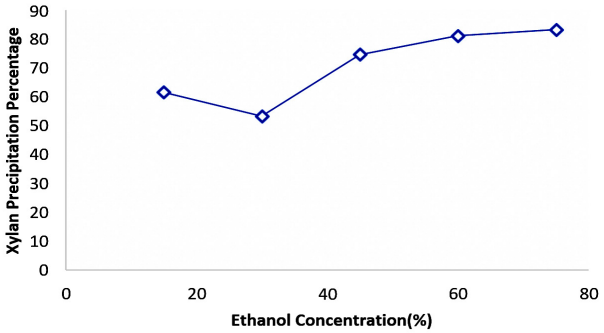

Fig. 4. The effect of ethanol concentration on xylan precipitation.

Biofilm preparation

Table 5. Water vapor permeability and tensile strength of film produces by different plasticizer.

Plasticizer	Water Vapor Permeability (g s^{-1} m^{-1} Pa)	Tensile Strength (MPa)
Glycerol	5.820	9
Sorbitol	4.855	29
Glycerol & Sorbitol	5.561	16

The extracted xylan was used to produce bio-polymer film. Two types of plasticizers were used for the film preparation and their effects on the film characteristic was showed in **Table 5**. Biofilm should control the water vapor permeability. In this study, film with glycerol addition resulted high water vapor permeability (5.82 g s^{-1} m^{-1} Pa) compared to glycerol/sorbitol (5.56 g s^{-1} m^{-1} Pa) and sorbitol (4.86 g s^{-1} m^{-1} Pa). This is due to the hydrophilic nature of glycerol that absorbs water [22]. For tensile strength, sorbitol gives higher tensile strength compared to other plasticizers. Similar results were found in the study. Therefore, sorbitol is a more effective ingredient than glycerol and a mixture of glycerol and sorbitol

CONCLUSION

From the analysis of the composition of oil palm fronds, it was found that oil palm frond contains (%) 30.8 ± 0.4 glucan, 19.3 ± 0.3 xylan and 18.4± 0.8 lignin. The percentage of extraction of xylan with sodium hydroxide is higher than sulfuric acid and dimethyl sulfoxide. Xylan extracted with dimethyl sulfoxide contains acetyl qualifiers and is suitable for producing carboxymethyl xylan. For xylan deposition, the use of a high concentration of ethanol gave a high xylan precipitation. Finally, the film with sorbitol as a plasticizing material showed low water absorption and high tensile strength of 4,855 $gs^{-1}m^{-1}$ Pa and 26 Mpa respectively.

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