

Isolation of Cellulosic Material from Agro-wastes and their Derivatization

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Abstract

Isolation of cellulosic materials from agricultural wastes such as skin of various fruits have been carried out. Isolated cellulosic materials have been converted into their acetate and carboxymethyl cellulose derivatives. The derivatives have been characterized by titrimetric method, pH titration and FT-IR spectroscopy. The characteristic features of these derivatives suggest the possibilities of their commercial utilization. Hence, this will reduce the environmental pollution and help to develop economy of the country.

Key words: Cellulose, Cellulose acetate, Carboxymethyl cellulose, Agro-wastes

I. Introduction

Bangladesh is rich in various seasonal fruits but skins of the fruits are barely used in our country. The skins of the various seasonal fruits are agricultural wastes which creates environmental pollution. Therefore, its proper utilization may help to have a friendly environment as well as it may help to affix our economic development. Skins of fruits might be used as a source of cellulosic material and isolation of cellulosic material and conversion into their derivatives may produce environment friendly product and also eliminate environmental pollution. Cellulose derivatives such as cellulose acetate is used¹ in textiles and clothing's, spectacle frames, tools and photographic films etc. and similarly Carboxymethyl cellulose (CMC) is used¹ in food science as a viscosity modifier or thickener and to stabilize emulsion in various products including ice cream. CMC is also a constituent of many non-food products such as personal lubricants, toothpaste, laxatives, diet pills, water based paints, detergents, textile sizing and various paper products etc. Derivatization of cellulosic material of fruits skins might be economically significant and remove waste disposal problem. Literature survey reveals that almost no work has been done on derivatization of cellulosic material isolated from various fruits skins available in Bangladesh. Hence, this paper deals with the isolation of cellulosic material and preparation of cellulose acetate and carboxymethyl cellulose and their characterization.

II. Experimental

Solvents and chemicals

All the solvents used in the present work were analytical grade (Merck and BDH). All the solvents were distilled before use.

Sample collection and preparation

The samples were collected from different places of Dhaka city. It was first cut into small pieces, dried in open air and finally dried in the oven below 45°C. The dried plant material was grinded with grinder mill and stored at room temperature to carry out the experiments.

Extraction of dried powder

Dried powder from skin of the fruits such as banana, mango, pineapple, coconut etc. were extracted separately with (500 mL) petroleum ether (b.p. 40–60°C) under reflux condition for 30 minutes. After refluxing, the content of the flask was allowed to cool at room temperature and filtered. The residue was dried in the air. This residue was marked as “extractive free powder”.

Delignification of extractive free powder²

Each of the extractive free powder (10 g) was suspended in water (200 mL) in a conical flask and heated at 70–80°C with constant stirring for 30 minutes in a magnetic stirrer. Then 2 g of Sodium chlorite was added into the conical flask followed by 15 mL glacial acetic acid dropwise. The addition of sodium chlorite and acetic acid were repeated four times. The percentages of yield of delignified powder (holocellulose) obtained from each extractive free powder was calculated and given in Table 1.

Isolation of α -cellulose³

Each of the dried holocellulose (3.0 g) was taken in a round bottom flask and sodium hydroxide solution (17.5%, 30mL) was added into the flask under nitrogen atmosphere. Then the mixture was stirred for about 4 hours using magnetic stirrer. Content of the flask was filtered with cloth filter and the residue was washed with distilled water followed by acetic acid. Then again it was washed with water followed by ethanol. Finally the residue was dried in air and percentage of α - cellulose was calculated and given in Table 1.

Preparation of cellulose acetate⁴

Holocellulose (1.08 g) obtained from each sample was taken in a round bottomed flask and placed in a magnetic stirrer for frequent stirring at 80°C for about 1 hour. After stirring, it was placed in a water bath at 60°C and a mixture of acetic anhydride (10 mL) and concentrated sulphuric acid (0.4 mL) was added into it dropwise from a dropping funnel for about 30 minutes at constant temperature. After addition of the mixture, the content of the flask was kept in water bath for another 30 minutes at the same temperature (60°C). The clear solution obtained at the bottom of the flask which was turned into curdy white precipitate after addition of distilled

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water. The precipitate of cellulose acetate (Scheme-1) obtained was centrifuged and washed with distilled water followed by ethanol. It was dried in air and percentage of yield was calculated and the results are given in Table 1.

*Determination of degree of substitution (DS) of cellulose acetate*⁵

Degree of substitution of the prepared cellulose acetate was determined by titrimetric method. An ethanolic solution of cellulose acetate was treated with sodium hydroxide solution and the volume of unreacted sodium hydroxide was measured by titration with standard hydrochloric acid. Degree of substitution of cellulose acetate was calculated and the results are given in Table 2.

*Preparation of carboxymethyl cellulose*⁶

Holocellulose of each sample (0.5 g) was taken in a round bottom flask and aqueous ethanolic (1:4) sodium hydroxide solution (15 mL) was added with continuous stirring by a magnetic stirrer for 2 hours at 30 °C. The flask was placed in thermostatic water bath with a condenser at 58 °C, and then 10 mL of 80 % monochloroacetic acid was added drop by drop through a dropping funnel with occasional stirring and then the content of the flask was left for 6 hours with reflux condenser. The flask was removed from the bath, cooled to room temperature and the content was centrifuged. The centrifuged mass was washed with 80% ethanol and finally with a mixture of 80% ethanol and 1 mL acetic acid. The carboxymethyl cellulose (Scheme-2) obtained was dried in air and percentage of yield was calculated and the results are given in Table 1.

*Determination of degree of substitution (DS) of carboxymethyl cellulose*⁷

Degree of substitution of each of the prepared carboxymethyl cellulose was determined separately by pH titration. Carboxymethyl cellulose sample was acidified by hydrochloric acid (0.5 M) until pH 3.15. Then acidic carboxymethyl cellulose sample was titrated by standard sodium hydroxide solution and pH was recorded upon the addition of sodium hydroxide solution with the help of pH meter. pH vs. volume of sodium hydroxide titration curves were prepared and analyzed using software CurTipot (pH and acid base titration curve Analysis & simulation) version 3.3.1 (2008) for MS Excel. The degree of substitution was calculated using following equation and results are given in Table 2.

$$DS = \frac{162 \ n_{\text{COOH}}}{m_{\text{ds}} \ 58 \ n_{\text{COOH}}}$$

where, 162 g/mol is the molar mass of an anhydroglucose unit (AGU), n_{COOH} (in mol) is the amount of COOH calculated from the volume of NaOH determined, 58 g/mol is the net increase in the mass of an AGU for each carboxymethyl group substituted and m_{ds} (in g) is the mass of dry sample.

FT-IR spectroscopic analysis of holocellulose, α -cellulose, cellulose acetate, and carboxymethyl cellulose

The FT-IR spectrum of each of the holocellulose, β -cellulose, cellulose acetate, and carboxymethyl cellulose

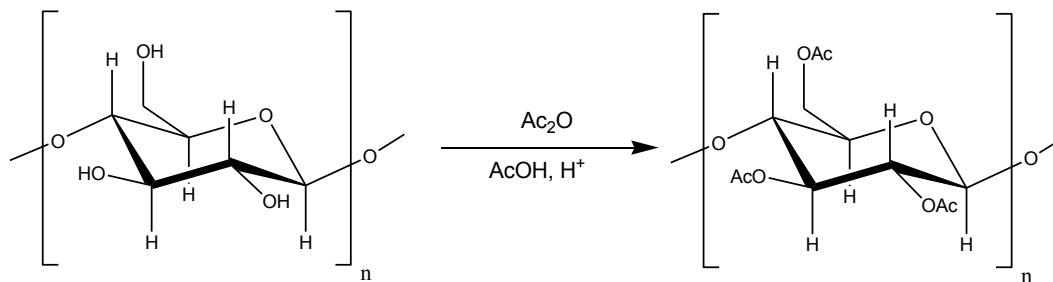
samples obtained from different agro-waste were recorded in KBr pellets using a Shimadzu FT-IR-470 Spectrophotometer. Characteristic IR-bands for holocellulose and β -cellulose were obtained at 3450-3400, 3000-2850 and 1100-1000 cm^{-1} , the characteristic IR-bands for cellulose acetate were found at 3450-3400, 1750-1730 and 1400-1000 cm^{-1} , and the characteristic IR-bands for carboxymethyl cellulose were observed at 3450-3400, 1725-1700 and 1400-1000 cm^{-1} .

III. Results and Discussion

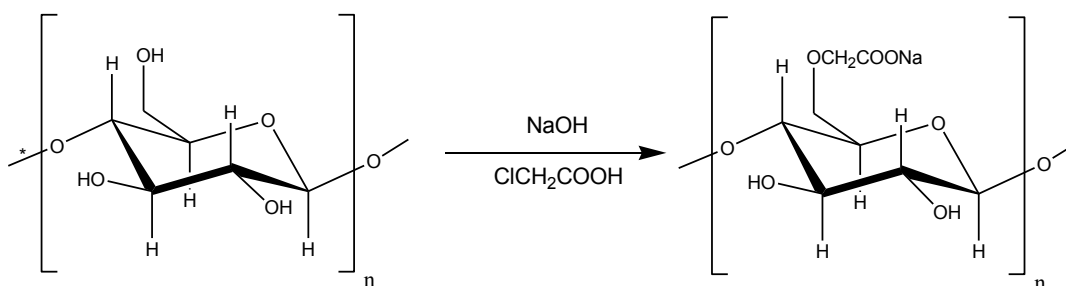
The agro-wastes such as skins of mango, banana, pineapple, and leaves of pineapple, outer shell of green coconut, outer shell of young palm, and Pumpkin peel were collected locally, cleaned, dried, and powdered. The powders were separately extracted with petroleum ether (b.p. 40-60°C). The extractive free powders were separately delignified¹ to obtain holocellulose. Then β -celluloses were obtained³ from holocelluloses separately. Each of the holocelluloses was separately acetylated⁴ and carboxymethylated⁶. Both of the acetate and CMC derivatives of holocellulose of the different samples were separately characterized^{5,7}. From the Table 1, it appears that the percentages of holocelluloses are highest in skin of mango (92.40 %) and lowest in outer shell of green coconut (53.21 %). The percentages of holocelluloses in other samples (Table 1) are closer to the higher value. The β -cellulose content is highest in outer shell of young palm (44.33 %) and lowest in leaves of pineapple (27.42 %). The percentage of β -cellulose for skin of banana (43.20 %), mango (39.70 %) and outer shell of green coconut (42.20 %) are very near to the higher value and that of leaves of pineapple is near to the lowest one. Therefore, it reveals that the skins of fruits contain significant percentage of cellulosic materials which are quite comparable to the cellulosic material of other common sources like cotton, jute, bamboo etc. These results indicate that these agro wastes might be used as the source of cellulosic materials. The percentage of converted cellulose derivatives from holocellulose of skin of fruits are quite satisfactory (Table 1). The degree of substitution (DS) of the cellulose derivatives estimated by titrimetric and pH metric titration for cellulose acetate and carboxymethyl cellulose, respectively. The DS values of cellulose acetate and carboxymethyl cellulose indicate that high percentage of cellulosic material have been converted into their derivatives (Table 2). DS value of acetate and CMC of cellulosic material varies with the source of cellulose although there is no direct relationship with the DS and extent of the derivatisation. Infrared spectral analysis of the holocellulose, peaks were found at 3450-3400, 3000-2850 and 1100-1000 cm^{-1} indicating the presence of O-H stretching, C-H stretching and C-O stretching of sugar unit, respectively, but no distinct peak for C=O stretching was found. On the other hand IR spectra of cellulose acetate and carboxymethyl cellulose indicated the strong absorption peak of >C=O of acetate group at 1750-1730 cm^{-1} , strong absorption peak of >C=O of carboxylate ion at 1725-1700 cm^{-1} , medium absorption peak of C-O stretching of carboxylate group at 1450-1300 cm^{-1} and medium absorption peak of C-O stretching of acetyl group at

1300–1200 cm^{-1} . The DS determination and IR spectral analysis indicated the successful acetylation and carboxymethylation of cellulosic material obtained from various

fruit skins. From the results it also appears that the derivatives obtained from the agro-wastes might be commercially used in terms of their property and quality.



Scheme 1: Preparation of cellulose acetate



Scheme 2: Preparation of carboxymethyl cellulose

Table 1. Percentage of cellulose isolated from waste materials and percentage yield of their derivatives

Name of the sample	Botanical name	Percentage of cellulose (%)		Percentage yield (%)***	
		Holocellulose*	α -cellulose**	Cellulose acetate	Carboxymethyl cellulose
Skin of banana	<i>Musa paradisiaca</i>	88.03	43.20	45.03	ND
Skin of mango	<i>Mangifera indica</i>	92.40	39.70	50.62	ND
Leaves of pineapple	<i>Ananas comosus</i>	91.65	30.46	74.77	85.95
Skin of pineapple	<i>Ananas comosus</i>	89.03	27.42	56.20	96.17
Outer shell of green coconut	<i>Cocos nucifera</i>	53.21	42.20	40.99	60.00
Outer shell of young palm	<i>Borassus flabellifer</i>	80.14	44.33	46.28	65.60
Pumpkin peel	<i>Cucurbita maxima</i>	67.59	50.49	44.62	68.84

* From extractive free powder; ** From holocellulose; ***From holocellulose

Table 2. Degree of substitution (DS) of cellulose acetate and carboxymethyl cellulose

Name of the sample	DS of cellulose acetate (%)	DS of carboxymethyl cellulose
Skin of banana	19.03	ND
Skin of mango	17.63	ND
Leaves of pineapple	40.28	0.83
Skin of pineapple	30.72	0.72
Outer shell of green coconut	26.53	0.70
Outer shell of young palm	16.50	0.48
Pumpkin peel	23.45	0.60

ND = Not done

Conclusion

The results suggest that agro-wastes (skins of different fruits) can be used as a potential source of cellulosic materials and the cellulosic materials of the agro wastes could be successfully converted into its derivatives (cellulose acetate and carboxymethyl cellulose), which can be used for different commercial and industrial purposes.

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