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Research Article

Isolation of Cellulosic Materials from Wastes of Fruits of Bangladesh and their Derivatization

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ABSTRACT

Cellulosic materials from various agro-wastes, 'such as outer skin of jackfruit (*Artocarpus heterophyllus* Lam.), non-edible part of jackfruit, inner stick of jackfruit, skins of lychee (*Litchi chinensis* Sonn.) and skins of lotkon (*Baccaurea ramiflora* Lour.)' have been isolated. Cellulose acetate and carboxymethyl cellulose have been prepared from those isolated cellulosic materials. The prepared derivatives have been characterized by FTIR spectroscopy, titrimetric method and pH-metric titration. The results indicate the possibilities of commercial utilization of the cellulose derivatives.

Keywords: Cellulosic material, Cellulose acetate, Carboxymethyl cellulose, Titrimetric method, Agro-wastes

INTRODUCTION

Bangladesh is rich in various seasonal fruits but there is no effective use of the outer skins and non-edible part of the fruits in our country. Non-edible part of the various seasonal fruits such as outer skin of jackfruit, skin of lycche and skin of lotkon etc are agricultural wastes which have low value in the environment. Therefore, proper utilization of these agro-wastes may help to have a friendly environment as well as it may contribute to economic development. Wastes of fruits might be used as a source of cellulosic material. Isolation of cellulosic material and conversion into their derivatives may produce high value end product and also eliminate environmental pollution. The cellulosic materials of agro-wastes might be partially or wholly modified by treating with various chemicals to produce wide range of end products known as 'cellulose derivatives'. The nitrates, acetates, carboxymethyls, xanthates, ethers etc. derivatives of cellulose have versatile and remarkable industrial uses [1-4]. Cellulose acetate is the most important derivative having multipurpose commercial application among all the cellulose derivatives. Acetate derivatives are generally used in the preparation of photographic films, plastic films, laquers, camera accessories, transparent sheeting, telephone, magnetic tapes and electric parts [5-7]. Carboxymethyl cellulose (CMC) is used in food science as a viscosity modifier or thickener, cosmetics, pharmaceutical and detergents industries[8]. Purified CMC is a white to cream colored, tasteless, odorless, freeflowing powder[9]. CMC has the ability to suspend solids in the aqueous media. It is also used for emulsion stabilization, moisture absorbtion from atmosphere, solubilization of proteins, thickening of solution and formation of films. CMC used as good enteric coatings for powders and tablets[8]. Derivatization of cellulosic material from outer skins and non-edible parts of fruits might be economically significant and as well as eliminates waste disposal problem. Literature survey reveals that almost no work has been done on derivatization of cellulosic material isolated from various agro-wastes available in Bangladesh. This research work is aimed at isolation of cellulosic material from agro-wastes and conversion into their derivatives such as cellulose acetate and carboxymethyl cellulose.

MATERIALS AND METHODS

Solvents and chemicals

All the solvents used in this research work were analytical grade (Merck and BDH). All the solvents

were distilled by fractional distillation before use.

Sample collection and preparation:
The samples, such as outer skin of jackfruit, non-edible part of jackfruit, inner stick of jackfruit, skin of lychee and skin of lotkon were collected from different places of Dhaka city. It was first cut into small pieces, dried in open air and finally dried in an oven below 45ºC. The dried samples were separately grinded with grinder mill and stored at room temperature to carry out all the experiments.

Extraction of dried powder:
Each of the dried powder samples was extracted separately with (500 ml) petroleum ether (b.p. 40−60ºC) 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 and marked as "extractive free powder". The percentages of yield was calculated for each sample and stored at room temperature to carry out the next experiments.

Delignification of extractive free powder[10]:
Each of the extractive free powder (10 g) was suspended in water (200 ml) in a conical flask and heated at 70−80ºC with constant stirring for 30 minutes in a magnetic stirrer. Then Sodium chlorite (2 g) was added into the conical flask followed by glacial acetic (15 ml) acid in drop wise. 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 the results are given in Table 1.

Isolation of α-cellulose[11]:
Each of the dried holocellulose (3.0 g) was taken in a round bottom flask and sodium hydroxide solution (17.5%, 30 ml) 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. The residue was further washed with water followed by ethanol. Finally the residue was dried in air and percentage of α-cellulose was calculated and the results are given in Table 1.

Preparation of cellulose acetate[12]:
Holocellulose (1.08 g) and α-cellulose (1.05 g) of each sample was taken separately in a round bottomed flask and placed in a magnetic stirrer for frequent stirring at 80ºC 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 drop wise 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 water. The precipitate of cellulose acetate obtained was centrifuged and washed with distilled water followed by ethanol. It was dried in air and percentage of yield of the cellulose acetate obtained from holocellulose and α-cellulose respectively, was calculated and the results are given in Table 1.

Determination of degree of substitution (DS) of cellulose acetate[13]:
Degree of substitution of the prepared cellulose acetate was determined by titrimetric method. Ethanolic solution of cellulose acetate was treated with sodium hydroxide solution and the volume of unreacted sodium hydroxide was measured by standard hydrochloric acid. Degree of substitution of cellulose acetate was calculated and the results are given in Table 2.

Preparation of carboxymethyl cellulose[14]:
Holocellulose and α-cellulose of each sample (0.5 g) was taken separately in a round bottom flask and aqueous ethanolic (80%) sodium hydroxide solution (18%, 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 monochloroacetic acid (10 ml of 80 %) was added drop by drop through a dropping funnel with occasional stirring and then the content of the flask was refluxed 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 ethanol (80%, 15ml) and acetic acid (1 ml). The carboxymethyl cellulose obtained was dried in air and percentage of yield was calculated on the basis of holocellulose and α-cellulose, respectively and the results are given in Table 1.

Determination of degree of substitution (DS) of carboxymethyl cellulose[15]:
Degree of substitution of each of the prepared carboxymethyl cellulose was determined separately by pH metric 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 value 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 and results are given in Table 2.

FTIR spectroscopic analysis of holocellulose, α-cellulose, cellulose acetate, and carboxymethyl cellulose:

The FTIR spectrum of each of the holocellulose, α-cellulose, cellulose acetate, and carboxymethyl cellulose samples obtained from outer skin of jackfruit, non-edible part of jackfruit, and inner stick of jackfruit, skin of lychee and skin of lotkon were recorded in KBr pellets using a Shimadzu FTIR-470 Spectrophotometer. Characteristic peaks for holocellulose and α-cellulose were obtained at 3450-3400, 3000−2850 and 1100−1000 cm^{-1}, the characteristic peaks for cellulose acetate were found at 3450-3400, 1750−1720 and 1400−1000 cm^{-1}, and the characteristic peaks for carboxymethyl cellulose were observed at 3450−3350, 1720−1700 and 1400−1100 cm^{-1}.

RESULTS AND DISCUSSION

The agro-wastes such as outer skin of jackfruit (*Artocarpus heterophyllus* Lam.), non-edible part of jackfruit, inner stick of jackfruit, skins of lychee (*Litchi chinensis* Sonn.), skins of lotkon (*Baccaurea ramiflora* Lour.), were collected from Dhaka city, cleaned, dried, and powdered. The powders were separately extracted with petroleum ether (b.p. 40−60^{o}C). The extractive free powders were separately delignified[10] to obtain holocellulose. Then α-celluloses were isolated[11] from holocelluloses separately. Each of the holocelluloses and α-celluloses was separately acetylated[12] and carboxymethylated[14]. Both of the acetate and CMC derivatives of holocellulose and α-cellulose of the different samples were separately characterized[13, 15]. From the Table 1, it appears that the percentages of holocelluloses are highest in skin of lotkon (89.71 %) and lowest in inner stick of jackfruit (60.10 %). The percentages of holocelluloses in other samples (Table 1) are closer to the higher value. The α-cellulose content is highest in outer bark of jackfruit (50.13 %) and lowest in skin of lychee (40.82 %). The percentage of α-cellulose in inner stick of jackfruit (47.70 %) is very near to the higher value and the percentage of α-cellulose in non-edible part of jackfruit (40.82 %) and skin of lotkon (42.33 %) are near to the lowest value. Therefore, it reveals that waste material 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[16]. These results indicate that these agro wastes might be used as the source of cellulosic materials. The percentage of converted cellulose derivatives from holocellulose and α-cellulose from wastes 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). 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.

CONCLUSION

This finding suggests that agro-wastes (outer skins and other non-edible parts of different fruits) might be used as source of cellulosic material and the cellulosic material of the agro waste could be successfully and significantly converted into its derivatives (cellulose acetate and carboxymethyl cellulose), which can be used for different commercial and industrial purposes.

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

Name of the sample	Percentage of yield (%)					
	Holocellulose	α-cellulose	Cellulose acetate		Carboxymethyl cellulose	
			Holo- cellulose	α-cellulose	Holo- cellulose	α-cellulose
Outer skin of jackfruit	88.54	50.13	58.52	45.09	74.93	81.06
Non-edible part of jackfruit	86.52	40.82	45.03	38.83	40.00	60.00
Inner stick of jackfruit	60.10	47.70	54.80	41.10	62.50	52.75
Skin of lychee	85.10	40.82	47.93	49.32	44.50	47.38
Skin of lotkon	89.71	42.33	51.98	41.22	42.60	41.05

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

Name of the sample	DS of cellulose acetate (%)		DS of carboxymethyl cellulose	
	From hollocellulose	From α-cellulose	From hollocellulose	From α-cellulose
Outer skin of jackfruit	23.84	21.63	0.70	0.40
Non-edible part of jackfruit	19.03	19.00	0.40	0.60
Inner stick of jackfruit	42.59	40.42	0.62	0.55
Skin of lychee	43.37	47.07	0.45	0.45
Skin of lotkon	47.07	40.65	0.41	0.40

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