Synthesis of Biodegradable Plastic from *Citrus reticulata* Peels

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Abstract: *In the modern society plastics play a vital role as packaging materials in almost all the sectors of day-to-day life. These plastics do not degrade easily as they are invulnerable to the microbial decomposition and thus persist for a long time in the environment. All these have caused tremendous harm to the environment. To solve this problem alternative methods for producing bio-based plastics are highly encouraged. Bio-based plastics are derived from natural resources. These bioplastics can be composed of a variety of materials such as starch, cellulose etc. The present study has been conducted to serve two purposes at a time. The first one is to make use of the fruit's wastes and second, production of the bioplastic from those wastes. The production process was made using simple laboratory techniques. Characterization methods such as Fourier transform infrared (FTIR) spectroscopy and biodegradability further confirmed the properties of the bio-based plastic.*

Keywords: Peels, Carbohydrate, FTIR, Biodegradable.

I. INTRODUCTION

The 21st century generation technologies focused on the production of bioplastic from waste sources/non-edible things that are in great demand. Many sources are there from which bioplastic can be produced such as potato waste, corn stover, mango seed, grape waste, pumpkin seed, sugar bagasse, coffee waste, banana waste, avocado seed, carrot waste, peanut husk, cereals straw and citrus fruit waste.The genus *Citrus* belonging to Rutaceae family consists of about 140 genera and 1300 species including some of the important fruit species such as *C. reticulata* (tangerine), *C. sinensis* (orange), *C. limon* (lemon), *C. paradise* (grapefruit) and *C. aurantifoila* (lime) (Singh et al., 1983).Juices are prepared from the fresh *Citrus* fruits and the peels are discarded as wastes (Manthey & Grohmann, 2001). From the past few years worldwide production of *Citrus* fruits has significantly increased and has reached 82 million tons. Therefore, every year a large amount of peel is produced. Citrus peel is a good source of pectin, molasses and limonene (Bocco, 1998).

Citrus reticulata is the hybrid fruit crop (*Citrus nobilis* Lour x *Citrus deliciosa* Tenora) grown in India, China and many other countries. India ranks 5th in *Citrus* fruit production (Devkota et al., 1982). During the winter season, a citrus fruit variety is grown in North Indian states (mainly in Punjab and Rajasthan) called as *Citrus reticulata* (Kinnow or Tangerine). It is processed into juices by the industry and fruit vendors. About 30 to 34% peel is obtained as a major processing by-product. The Kinnow peel is a rich source of Vitamin C, carotenoids and polyphenolic antioxidants (Anwar et al., 2008)fat, protein, magnesium, ash, polyphenols, carotenoids and dietary fibres (Rincon et al., 2005). Here, in the present study the peels of *Citrus reticulata*have been considered for preparing the bioplastic.

II. MATERIALS AND METHODS

2.1 Methodology for determining the presence or absence of carbohydrates-

Carbohydrates are biological molecules consisting of carbon, hydrogen and oxygen atoms [1].

The Empirical formula is $(CH_2O)_n$, where n is the number of repeated units. Carbohydrates are divided into three main classes depending upon the complexity and behaviour on hydrolysis such as monosaccharides, oligosaccharides and polysaccharides. The word "saccharide" is derived from the Greek word sakcharon, meaning sugar [2].High carbohydrate content of a substance makes it a better source of bioplastic (Lusiana et al., 2019). Thus, before the peels of *Citrus reticulata* were choosen for making bioplastic, tests for carbohydrates were conducted to find the presence or absence of them in the peels. The standard protocol ofJahangirpuria et al. (2017) was followed for performing the tests.

2.2 Preparation of the Extract

10 mg boiled peels were dissolved in 10ml of distilled water.

A. Molisch's Test

Procedure: In the test tube, take 2ml of extract to this add 2-3 drops of alpha-naphthol solution. To this add slowly 1ml of concentrated Sulphuric acid.

B. Benedict's Test

Procedure: In the test tube, take 1 ml of extract to this add5ml of Benedict's solution. Place the test tube in a boiling water bath for 3 minutes and then allow it to cool.

C. Bradford's Test-

Procedure: In the test tube, take 2ml of extract to this add 2ml Bradford's reagent. Place the test tube into a boiling water bath for 3 minutes and then allow it to cool.

2.3 Production of the Bioplastic Film-

The production of the bioplastic film has been broadly divided into 2 main steps. The first one is the preparation of peels for using it as a base material and second one is the formation of the bioplastic from the peels.

Step 1- Preparation of *Citrus reticulata* Peels

The preparation has been conducted according to the protocol of Azieyanti et al.(2020). The fruits of *Citrus reticulata* were bought from a local market of Ahmedabad. The peels were acquired after the consumption of the fruits.These were cut into pieces and were put for boiling in a pan containing water. The peels were boiled for 45 minutes. After this they were taken out from the pan and left for drying on filter paper for about 30 minutes. After this the peels were placed in a blender and were blended until a uniform mixture was obtained.

Step 2- Production of bioplastic film from *Citrus reticulata* peels:

The bioplastic film preparation has been conducted according to the protocol ofSaraswat et al. (2014). 50 grams of the blended peel were weighed and placed in a non-stick pan with addition of 120ml of water. To this 10 ml of 0.1N HCl was added and stirred using a glass rod. Further 10ml of 0.1N NaOH and 4ml glycerol was added to the mixture.The mixture was stirred for about 15 minutes on low flame. Following this an aluminium foil was taken and it was greased with Vaseline uniformly. The mixture was poured on the foil maintaining uniform thickness.This was left for drying for about 2-3 days at room temperature.

Functions of the Ingredients taken has been mentioned below-

1. Hydrochloric acid (HCl) - breaks down amylopectin and changes the structure and properties of the polymer.
2. Sodium Hydroxide (NaOH) - neutralises the mixture.
3. Glycerol –acts as plasticizer.

2.3.1. Characterization of the Bioplastic

Based on the produced bioplastic colour, texture, transparency and odour was determined.

2.3.2. FTIR Analysis

FTIR analysis was conductedusing a spectrometer Bruker (alpha)for both the samples i.e., the bioplastic prepared from the *Citrus reticulata* peels and the zip pouch of 60 micron (Supercom Online) which was used for comparing the functional groups between the two samples. The spectral scanning range was from 4000cm^{-1} to 400 cm^{-1}.

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2.3.3. Biodegradability Test

Soil burial method was carried out for biodegradation of the bioplastic film. One 250 ml glass jar was used for the test; in the glass jar a cut piece of the bioplastic was kept with dimensions 3 cm x 3 cm. At a depth of 5cm the cut piece was placed and was further covered with soil. Following this water was sprinkled to keep the soil moist. After 24 hours, the soil was removed from the jar and placed into a plastic tray to check the condition of the bioplastic film.

III. RESULTS

3.1 Test for Carbohydrate presence-

In this work, *Citrus reticulata* peels were used for making bioplastic film and before the test was conducted presence of carbohydrates were evaluated on a preliminary basis. The results are as follows:

Table 1: Qualitative tests for finding the presence of carbohydrates

No.	Test	Observation	Inference	Reaction
1.	**Molisch's test**	A deep violet colour is produced at the junction of the two layers.	It shows presence of carbohydrates.	It is due to the formation of unstable condensation product of alpha-naphthol with furfural (produced by the dehydration of carbohydrate).
2.	**Benedict's test**	Formation of red, green or yellow precipitate.	It shows presence of reducing sugars.	If the saccharide is a reducing sugar, it will reduce copper Cu (II) ions to Cu(I) oxide, and form red precipitates.
3.	**Bradford's test**	A deep blue colour is formed with red precipitates settling down at the bottom or at sides of the test tube.	It shows appearance of reducing sugars. If the ppt. formation takes time, then it shows the presence of reducing disaccharides.	If the saccharide is a reducing sugar, it will reduce Copper Cu(II) ions to Cu(I) oxide.

The result from the above table clearly depicts the presence of carbohydrates in the *Citrus reticulata* peels.

3.2 Bioplastic Features

The bioplastic film was prepared from the peels along with addition of some chemicals such as hydrochloric acid and sodium hydroxide and glycerol. Fig 1 represents the prepared bioplastic film.

3.2.1. Characterization of the bioplastic prepared are discussed below:

1. **Colour:** The colour of bioplastic varies from source to source. In this experiment, *Citrus retciulata* peels were used hence, the bioplastic developed was of yellowish-orange colour.
2. **Texture:** Texture of the bioplastic film can be determined by touching the surface. The complete blended mixtures of the peels lead to a smooth texture from the bottom and rough texture from the top surface.
3. **Transparency:** Almost all bioplastics are transparent but some are semi-transparent. Here in the current experiment the bioplastic film made from *Citrus reticulata* peels wassemi-transparent.
4. **Odour:** The odour of the bioplastic was same as the Kinnow fruit, but due to the application of different chemicals the pungency got reduced.

Fig 1: Prepared Bioplastic film

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3.2.2. FTIR Analysis

The FTIR results has been represented as follows-

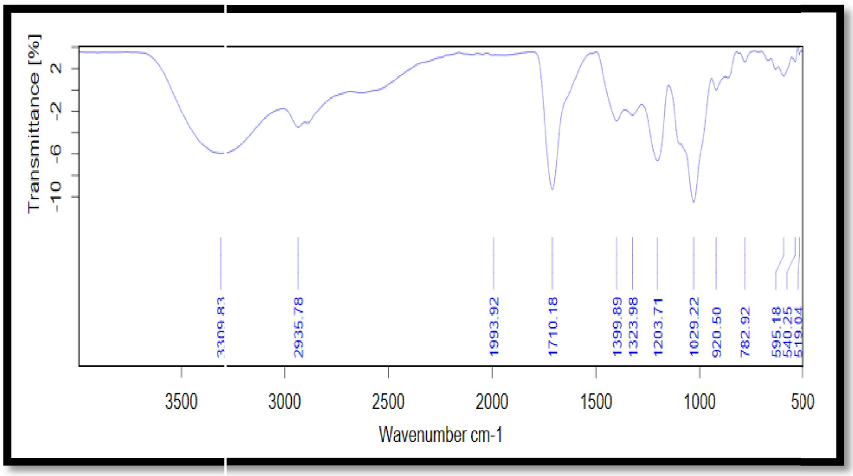

Fig 2:FTIR spectrum of the bioplastic derived from the *Citrus reticulata* peels

Table 2: FTIR spectrum analysis of the bioplastic derived from the *Citrus reticulata* peels

S. No.	Wave Number (cm^{-1})	Frequency Range	Appearance	Functional Group	Compound Class
1	3309.83	4000-3000 cm^{-1}	Medium	N-H Stretching	Aliphatic Primary Amine
2	2935.78	3000-2500 cm^{-1}	Medium	C-H Stretching	Alkane
3	1993.92	2000-1650 cm^{-1}	Weak	C-H Bending	Aromatic Compound
4	1710.18	2000-1650 cm^{-1}	Strong	C=O Stretching	Aliphatic Ketone, Carboxylic acid, Conjugated acid, Conjugated aldehyde
5	1399.89	1400-1000 cm^{-1}	Medium	O-H Bending	Carboxylic acid, alcohol
6	1323.98	1400-1000 cm^{-1}	Medium	O-H Bending	Phenol
7	1203.71	1400-1000 cm^{-1}	Medium	C-N Stretching	Amine
8	1029.22	1400-1000 cm^{-1}	Strong	C-F Stretching	Fluoro Compound
9	920.50	1000-650 cm^{-1}	-	-	-
10	782.92	1000-650 cm^{-1}	-	-	-
11	595.18	-	-	-	-
12	540.25	-	-	-	-
13	519.04	-	-	-	-

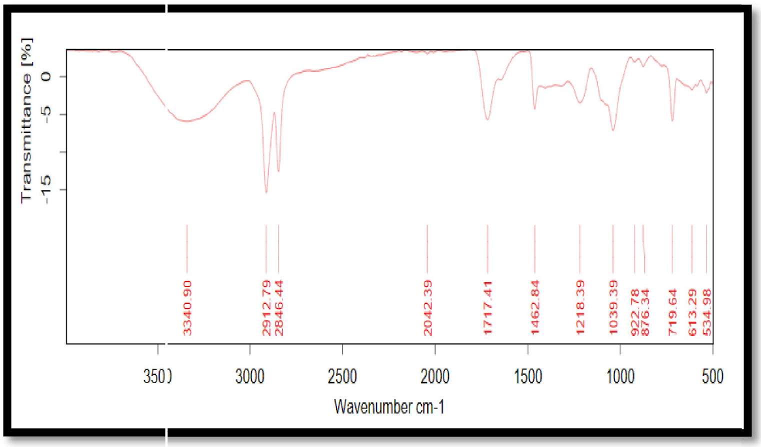

Fig 3: FTIR spectrum of the plastic zip pouch of 60 microns (Supercom Online)

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Table 3: FTIR spectrum analysis of the plastic zip pouch of 60 microns (Supercom Online)

S. No.	Wave Number (cm-1)	Frequency Range	Appearance	Functional Group	Compound Class
1	3340.90	4000-3000 cm^{-1}	Medium	N-H Stretching	Aliphatic primary Amine, Secondary Amine
2	2912.79	3000-2500 cm^{-1}	Medium	C-H Stretching	Alkane
3	2846.44	3000-2500 cm^{-1}	Medium	C-H Stretching	Alkane
4	2042.39	2400-2000 cm^{-1}	-	-	-
5	1717.41	2000-1650 cm^{-1}	-	-	-
6	1462.84	1600-1300 cm^{-1}	-	-	-
7	1218.39	1400-1000 cm^{-1}	Medium	C-N Stretching	Amine
8	1039.39	1400-1000 cm^{-1}	Medium	C-N Stretching	Amine
9	922.78	1000-650 cm^{-1}	-	-	-
10	876.34	1000-650 cm^{-1}	-	-	-
11	719.64	1000-650 cm^{-1}			Benzene derivative
12	613.29	1000-650 cm^{-1}	-	-	-
13	534.98	1000-650 cm^{-1}	-	-	-

The FTIR analysis of the bioplastic derived from the *Citrus reticulata* peels showed principle compound classes-alkane, alcohol, amine, aliphatic primary amine, aromatic compound, aliphatic ketone, carboxylic acid, conjugated acid, conjugated aldehyde, fluoro compound and phenol. Whereas, the FTIR analysis of the plastic zip pouch showed principle compound classes-alkane, amine, aliphatic primary amine, secondary amine and benzene derivative. Hence, the common compound classes that were found in both the samples were alkane, amine, aliphatic primary amine. Alkanes are most basic of all hydrocarbons [3] and most plastic come from hydrocarbons that are further derived from crude oil, natural gas and coal [4]. Amines protect plastics against radical oxidative degradation and ozonation (Pospisil et al., 1995). The difference of the compound classes in both the samples further reveals that two samples have different properties.

3.2.3. Biodegradability Test

It was observed from the biodegradability test that the prepared bioplastic film got completely degraded in the soil. The sprinkling of water enhanced the enzymatic activities of the microorganisms of the soil. The carbohydrate constituents present in the *Citrus reticulata*peel provide carbon sources which further helped in growth and multiplication of the soil microorganisms (Yaradoddi et al., 2022).

IV. DISCUSSION

Bioplastic has been chosen as an alternative for the synthetic plastics that people around the world are using. These bioplastics are derived from different biological resources like starch from corn, tapioca, cassava, wheat, rice, etc. which are eatable products (Saraswat et al., 2014). The world population is increasing and there are many people who don't even get food on daily basis. Considering this reason, it has been extremely necessary to find out non-eatable products to make these biodegradable plastics. Researchers throughout the world have prepared bioplastic using fruit peels of banana, orange, apple pomace etc. encouraging further work in this field.

Before the current experiment, preliminary test for the presence of carbohydrate was done for finding out whether the experiment can lead in production of the bioplastic. Carbohydrate is divided into 3 subtypes which further forms the base material for producing bioplastics.

Molisch's, Benedict, and Bradford tests were performed to confirm the presence of carbohydrates. On the basis of literature review it was found that before the current experimental work no author has reported such tests to confirm carbohydrates in the peels of the fruits chosen for their experimentation purpose.

Similar experiment was conducted by (Yaradoddi et al., 2022; Marsi et al., 2019). But orange peels were considered for preparing the bioplastic film while in the present experiment peels of *Citrus reticulata* has been considered for the preparation of the bioplastic film. Hence, this makes the preparation of the bioplastic film unique. The degradation test suggested that the prepared bioplastic was environment friendly.

V. CONCLUSION

Worldwide scientists are trying to find alternatives of the synthetic plastics as they have caused tremendous amount of pollution. Finding alternatives can save the earth from getting further deteriorated. Keeping this in mind the present experiment was conducted. In the current experiment the bioplastic was prepared using the fruit waste i.e., peels and very few ingredients, which makes it a reliable and economically convenient material to be used in future. The bioplastic degraded very easily. The carbohydrate constituents that were present in the *Citrus reticulata* peels enabled the bioplastic to degrade and proved that in future it can be of great help as a short-live packaging material. In future progress this can evolve into an appropriate replacement of the conventional synthetic plastics. Further researches can help in increasing the shelf-life of the bioplastic.

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