

Physicochemical characterization of two varieties of oranges peels and evaluation of its potential in biodegradable plastic films formulation

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Abstract

The use of plastics from non-biodegradable fossil resources is a major source of pollution. As a result, fossil resources are gradually being replaced or reinforced by renewable resources such as: agropolymers, polymers from microorganisms and biotechnology in the manufacture of ecological plastics. Our study therefore proposed an effective solution to this problem via the valorization of agropolymers from orange peels in bioplastics. The physicochemical parameters of two varieties of orange peel grown in Benin (*Valencia* and *Pineapple*) were determined by following international standard protocols. From the obtained results, it appears that the pH of orange peels is comprised between 3.59 and 4.04; orange peels are acidic and constitute a pollution factor for the environment. The peels are also rich in cellulose (19.08% for *Valencia* and 19.76% for *Pineapple*). The pectin content is 23.5% in the peels from *Valencia* variety while that of the *Pineapple* variety is 22.00%. Lignin content ranges 4.75% to 6.93%. These fibers' contents show that orange peels are a potential source of biomass that can be used as reinforcement material in the formulation of bioplastics.

Our future work will focus on the formulation of biodegradable plastic films using the characterized orange peel.

Keywords: *Pineapple*; *Valencia*; Orange peels; Physicochemical parameters; Bio plastics

1. Introduction

From the citrus family, the orange tree (*Citrus sinensis*) is one of the crops in the world whose fruits are widely consumed. Its production has continued to increase each year and was 70.45 Megatons in 2013 [1]. In Benin, citrus fruits are not only the second fruit grown and marketed after pineapple (*Ananas comosus*) but also the third most consumed fruit after mango (*Mangifera indica*) and banana (*Musa spp*) [2]. The orange tree sector in Benin is booming with overproduction in September/October and an average annual income per producer estimated at 2262.44\$US in 2014 [3] [4]. Orange peel waste, estimated at 15.56 Megatons per year [5] with a low pH, high organic matter content [6] thus pollutes the environment. It is therefore necessary to recycle the waste (peel) of the orange.

Previous work has focused on the recovery of orange waste. From this work, it appears that orange peel (*Citrus sinensis* L.) is rich in antioxidant compounds [7]. The study on the functional physicochemical properties of phenolic acids from raw and dried orange and lemon peels revealed their potential use as sources of ingredients in food fortification [8].

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Used as raw material in the manufacture of animal feed, orange peels are also used to synthesize adsorbent material to remove organic pollutants via adsorption on natural materials [9]. They are reinforced by the epoxy composite in the production of biobased polymer loaded with magnetized ferrite [10]. Similarly the cellulose derived from these barks is used to reinforce the poly-(vinyl alcohol), PVA. The plastic film thus obtained has a higher tensile strength and modulus of elasticity than the commercial PVA/microcrystalline cellulose blend film [11].

However, the use of orange peels in the design of agro-materials that can replace plastics remains to be explored. Accordingly, the present study aims to evaluate the physicochemical parameters of the peels from two main orange varieties cultivated in Benin, for the production of biodegradable plastic films.

2. Material and methods

2.1. Plant material

Two varieties of oranges (*valencia and pineapple*) were selected and purchased from the SEDJLO fruit garden in Za-kpota / Zou-Bénin (figure 1).

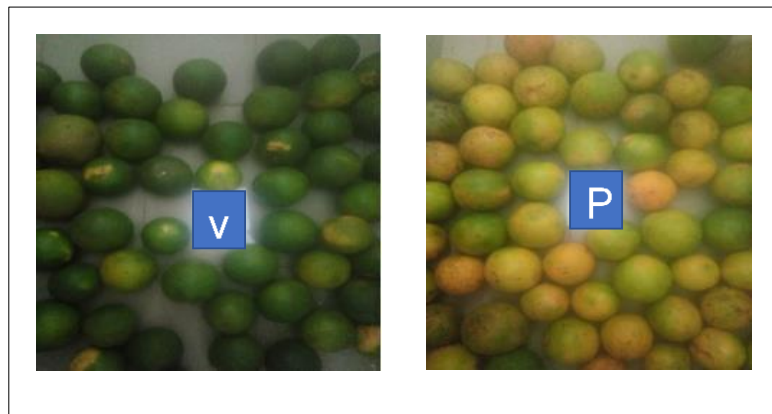


Figure 1 Image of the studied two varieties of orange ((P=*Pineapple* and V=*Valencia*)

2.2. Methods

2.2.1. Isolation, drying and grinding of orange peels



Figure 2 Isolation and grinding of orange peels a) orange peel; b) cut bark; c) determination of the Brix degree; d) dried and ground bark

The orange peels were gently isolated, cut into small pieces. The peels obtained were washed and soaked in tap water for 12 hours until they were bland, in order to eliminate all undesirable substances such as dirt and soluble sugars contained in. After obtaining washing water at 0 Brix, the peels were dried at room temperature for a week and grounded in the form of a powder using a grinder, and then stored in a hermetically sealed bottle to avoid humidity of the air (figure 2).

2.2.2. Physicochemical characterization of orange peel

Moisture content TH

The moisture content is determined according to the official AACC standard (1995) by drying 1 g of powder (contained in previously dried porcelain crucibles) in a CARBOLITE muffle furnace series no. 20-802568 type CTF 12 / 65 / 550. The vacuum crucible is first cleaned, dried and weighed (M_0). The crucible containing the sample is weighed again (M_1) and dried at 105 °C for 3 hours. After drying, the crucible and sample assembly was cooled in a desiccator before being weighed (M_2).

$$T_H = \frac{M_1 - M_2}{M_1 - M_0} \times 100 \text{ (in g/100g of substance)}$$

Dry matter content (T_{MS})

The dry matter content is related to the moisture content by the following relationship:

$$T_{MS} = 100 - T_H$$

Ash content

The ash content was determined according to standard NF V 03-909 (1988). The crucible containing the dried sample was put in the oven at 550 °C until ashes visibly free of carbonaceous particles were obtained. The crucible was cooled in a desiccator to room temperature and weighed quickly (M_3). The ash content (T_C) was determined from the formula:

$$T_C = (M_3 - M_0) \times \frac{100}{M_S}$$

2.2.3. Organic matter content

The organic matter content is related to the ash content by the following relationship:

$$T_{MO} = 100 - T_C$$

Hydrogen Potential (pH)

pH measures the concentration of hydrogen ions in a solution. It determines the acidic or basic character of an aqueous solution. The more acidic the solution, the lower the pH value and vice versa. The pH of orange peel in aqueous solution with a ratio of 1:10 was determined according to the MA method. 100 - pH 1.1 using a Hanna HI-8014 portable pH meter

Determination of titratable acidity

The determination of titratable acidity was made according to standards NF V 05-101 January 1974 and European standard EN 12147 December 1996. It is expressed in milliequivalents, for 100 g of product and is obtained by the following equation:

$$\text{Acidity} = N \times V_1 \times \frac{50}{V_0} \times \frac{100}{m}$$

Where;

N is the normality of the soda used V1 is the volume in milliliters of the sodium hydroxide solution;

m is the mass in grams of sampled product.

50 is the final volume of the solution in the volumetric flask;

V₀ is the volume in millilitres, of the aliquot test portion of the solution

It is also possible to conventionally express the titratable acidity in grams of acids per 100 g by multiplying the previous formula by the factor corresponding to the acid. The factor corresponding to monohydrated citric acid is 0.070.

Specific lipid content

The method used for the determination was continuous extraction by Soxhlet with hexane according to standard NF EN ISO 659 (1998). A mass $M_1 = 15$ g of each sample was weighed and then transferred to a cellulose cartridge placed in the extractor. A volume of 150 mL of hexane, contained in the empty weighed flask (M_2) is used for the extraction which lasts 7 h. The extract obtained is evaporated to dryness using a rota evaporator at 40°C and at the end the flask containing the lipids is weighed (M_3).

The lipid content (TL) is determined according to the relationship:

$$T_L = (M_3 - M_2) \times \frac{100}{M_1}$$

With

M_1 the mass of the sample (in g);

M_2 the mass of the empty balloon (in g) and

M_3 the mass of the balloon containing the lipids after evaporation (in g).

Protein content

The protein content was determined according to the French standard NF EN ISO 5983 (2005) by the Kjeldhal method. This method consists of mineralizing the organic nitrogen contained in the sample to obtain an ammonium salt. In the presence of an alkaline solution, this salt releases ammonia which is then trapped and quantified by an acid-base assay. Thus, the protein content is determined according to the formula:

$$\%Protein = \frac{\%Nitrogen}{\alpha} = \frac{(V_{eq} - V_{blank}) \times Titr_{HCl} \times M_{Nitrogen}}{m_{test} \times \%MS \times \alpha}$$

With;

α , the average nitrogen content in proteins estimated by default at 16% nitrogen in proteins;

V_{eq} is the equivalence volume of the sample during the titration;

V_{blank} is the volume of the blank during the test;

HCl titer is the normality of hydrochloric acid;

M nitrogen is the molar mass of nitrogen;

m test socket is the test socket mass;

$\%MS$ is the dry matter percentage of the sample.

Pectin content

The extraction of the pectin by hydrochloric acid was carried out according to the method adapted from Mourgues et al., 1983 [12]. Pectin is extracted from orange peels in a hot acid solution. The orange peel powder (1 g) is added to a solution of 40 mL of 0.1 N hydrochloric acid then boiled in a reflux system at 70 to 80°C for 4 hours. The mixture obtained is immersed in ice in order to stop the hydrolysis process.

The pectic juice is recovered after filtration and then clarified by centrifugation for 30 minutes at 4000 rpm. The pectin is then precipitated with two volumes of alcohol (95% ethanol) for one volume of filtrate. The precipitate is then collected and then dried at 40°C. The pectin content (T_p) is expressed in g/100 g of orange peel according to the equation:

$$T_p = (M_3 - M_2) \times \frac{100}{M_1}$$

In this relationship:

M_1 represents the mass of the sample (in g);

M_2 represents the mass of the empty filter (in g);

M_3 represents the mass of the filter containing the pectin after drying (in g).

Lignin, cellulose and hemicellulose content

- Pretreatment

We carried out a pretreatment using the “TAPPI T 204” standard, i.e. using 2 volumes of toluene for 1 volume of ethanol. This represents around 134 mL of ethanol for 266 mL of toluene. For this, a mass M_0 of the sample is introduced into a previously dried and weighed cartridge. Then the cartridge is inserted into the soxhlet then the extraction is done until a clear solvent is obtained in the soxhlet. At the end of the extraction, the sample was wash with ethanol and hot water then the cellulose cartridge was put in the oven at 60°C and weigh. The extractable content is determined by the formula:

$$\% \text{ Extractable} = (M_2 - M_1) \times \frac{100}{M_0}$$

With M_0 the mass of the sample; M_2 the mass of the cartridge containing the sample before extraction (in g) and M_1 the mass of the cartridge containing the sample after evaporation (in g).

- Lignin content

The lignin content was determined according to the TAPPI T 222 standard.

A mass $M_0 = 0.6$ g of the previously treated sample is introduced into a 500 mL flask. 10 mL of H_2SO_4 72p are added to it, to which 350 mL of distilled water are added after magnetic stirring for 2 hours. The mixture obtained is heated under reflux with continuous stirring. After 4 hours this mixture is left to cool and stand overnight or for a longer period for the lignin to settle. Then the lignin is quantitatively recovered on an M_1 mass filter and rinsed with heated distilled water until clear water is obtained after filtering. The filtrate obtained is dried at 105° C. for 24 hours then weighed (M_2).

$$\% \text{ lignine} = \frac{M_2 - M_1}{M_0} \times (100 - \% \text{ Extractable})$$

- Holocellulose content

Holocellulose is made up of cellulose and hemicellulose. To obtain it, the lignocellulosic residue from the pretreatment was delignified [13]. For this, a mass $M_0 = 1$ g of the pretreated sample is introduced into a flask then 75 mL of 0.2 N acetic buffer is added. To this mixture heated between 75°C and 80°C, 1g of sodium chlorite ($NaClO_2$) and 0.2 mL of glacial acetic acid until complete delignification, at least four chlorinations. Then the mixture is left to stand in an ice bath for 2 hours. After filtration using a dry mass M_1 filter and rinsing with distilled water (500 mL) and acetone (30 mL), the filter is dried for 24 hours at 40°C and weighed (M_2). The holocellulose content is determined by the expression:

$$\% \text{ Holocellulose} = \frac{M_2 - M_1}{M_0} \times (100 - \% \text{ Extractable})$$

- Cellulose content

The cellulose assay was performed as below from the holocellulose samples [14]:

1g of holocellulose is treated with a 17.5% sodium hydroxide solution (50 mL) for 30 min; then 50 mL of distilled water is added to the previous solution and an 8.75% sodium hydroxide solution is obtained. After reflux treatment, the cellulose obtained is filtered and rinsed with a 1% acetic acid solution (50 mL) then with distilled water (100 mL); the filtrate is dried at 40° C. for 24 hours and a pure cellulose in the form of α -cellulose is thus obtained.

The cellulose content is given by the relationship:

$$\text{Cellulose content} = \frac{\text{mass of dry precipitate}}{\text{masse of dry holocellulose}} \times 100$$

- Hemicellulose content

The hemicellulose content is determined by difference:

$$\% \text{ Hemicellulose} = \% \text{ Holocellulose} - \% \text{ Cellulose}$$

3. Results and discussion

3.1. Organic and mineral matter content

Water has a major impact on the structure, appearance, taste and breakdown of food. The water content of a sample affects its preservation and may be responsible for certain sample reactivity. Thus, drying at room temperature was evaluated by determining the moisture content of *Valencia* and *Pineapple* orange peels. The ashes obtained after calcination of the orange peels at high temperature are inorganic residues which represent the total mineral compound content of the sample. The results obtained are shown schematically in Figure 3. These results show that the two varieties studied were organic matter-rich, around 90% in dry and organic matter.

The *Valencia* variety has the highest moisture content at 8.85% which is the same range with that reported by Boudraa and Benali, around 8% [15]. These levels of water content would favor the preservation of crushed peels.

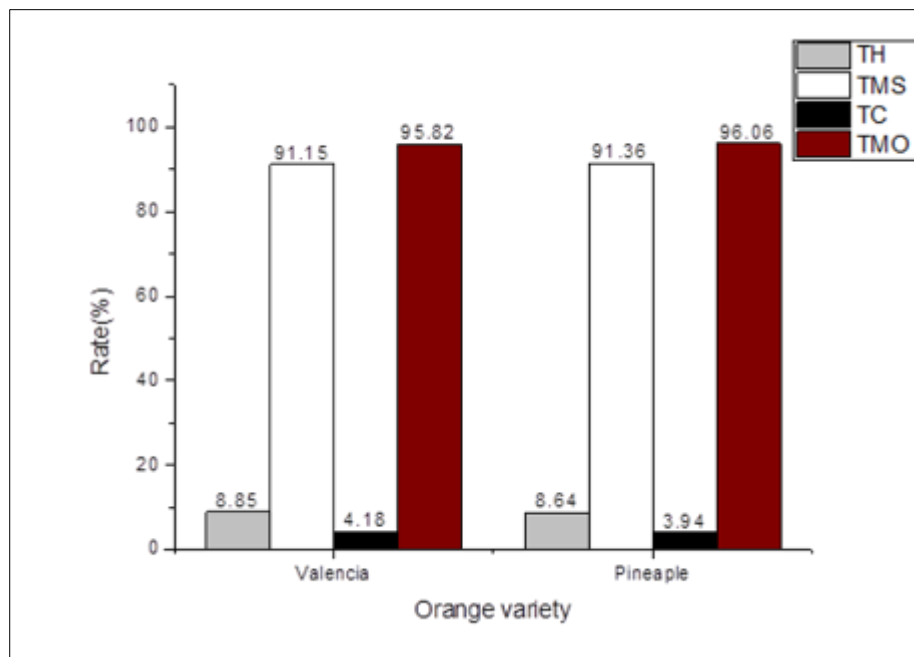


Figure 3: Organic and mineral matter content, TH=water content, TMS=dry matter content, TC=Ash content, TMO=organic matter content

3.2. Hydrogen Potential

The measured pH of the *Pineapple* variety was 3.59. This denoted that it is stronger acidic compared to *Valencia* variety with a pH equal to 4.04. The values obtained are close to the pH of by-products from the orange processing industry, between 3 and 4 [6]. However, the pH of an orange peel is equal to 5.25 according to the work of M'hiri (2016) [16]. This difference in pH may be due to the water/peels ratio used for pH measurement. Acidic orange peels are therefore a factor polluting the environment. This acidity is better appreciated by determining the titratable acidity of these peels.

3.3. Determination of titratable acidity

The values of the titratable acidity of orange peels indicated in Figure 4 provide better information on the nature of the peels than the pH. These values of the titratable acidity of *Valencia* and *Pineapple* peels are respectively 2.98 and 3.38 g equivalent of monohydrated citric acid per 100 g of peels. The peels of *Pineapple* variety is more acidic than that of *Valencia*. This conclusion agrees with that made previously based on the Hydrogen Potential. The values obtained are close to 2.1 g/100 g, titratable acidity of orange pulp as reported by Karadeniz (2004) [17]. Citric acid from orange peels can be used as a co-plasticizer in the production of composite starch film.

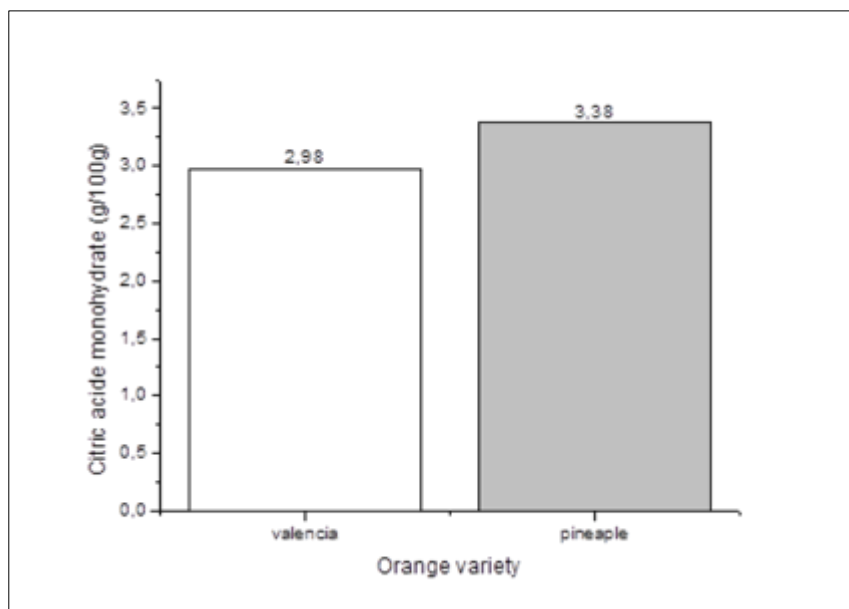


Figure 4 Titratable acidity of orange peels

3.4. Fat and protein content

Polymers in oils (lipids) and proteins have specific properties that justify their applications in food packaging, galenic, paint and varnish [18]. As a result, the lipid and protein contents of the orange peels were determined. The results obtained are collated in the table below. From this Table 1, it appears that *Valencia* and *Pineapple* orange peels contain low lipids with respective contents of 1.84 and 2.00%. It is found that the extraction yield is better compared to some previous works [19],[20],[21]. The size of the ground peels studied (less than 500 micrometers) and their varieties may be responsible for this observation. Similarly, the protein contents obtained are low.

Table 1 Fat and protein content

Orange varieties	Fat content	Protein content
<i>Valencia</i>	1.84 ± 0.26	1.108 ± 0.444
<i>Pineapple</i>	2.00 ± 0.09	0.875 ± 0.293

3.5. Determination of fiber contents

The fiber contents, in particular cellulose, hemicellulose, lignin, and pectin, were determined and the results obtained are shown schematically in Figure 5. These results indicate that the *Valencia* and *Pineapple* peels have respectively 20.89% and 24.52% extractables, materials not derived from their plant walls. These peels are therefore rich in lignocellulosic residues and can be transformed into value-added products such as bioplastics, filtration and water treatment membranes, second-generation biofuels and food additives [22].

The pectin contents vary between 22 and 23.5%. The greatest value is obtained with *Valencia* peels. These results are substantially in line with those obtained by Panwar et al., 2021 as well as Boudraa and Benali (2017) which are respectively 23.02 and 25.66% [15], [23]. These pectins can be used in the food industry (dairy products, ice creams and emulsified products, jams and jellies) and pharmaceuticals (manufacture of detoxification, anti-diarrheal, anti-cancer drugs) [16].

The cellulose contents of the two varieties *Valencia* and *Pineapple* are respectively 19.08% and 19.76%. These values are around 20% like those obtained by Ng (2019) [11]. On the other hand, there is a significant difference between our values and those obtained by Panwar et al., 2021. This difference is certainly linked to the age, the growing conditions and the climate of the plant species [24].

Orange peels have a lignin content of between 4.75 and 6.93%. However, modified lignin (lignosulfonates) acts as a dispersing agent, binder, plasticizer or complexing agent and reinforcement in synthetic polymer matrices [25]. So

lignin can be used in the formulation of plastic film from orange peels. These fiber contents obtained justify the use of orange peels in the production of biodegradable plastic films which will be the subject of our next publications.

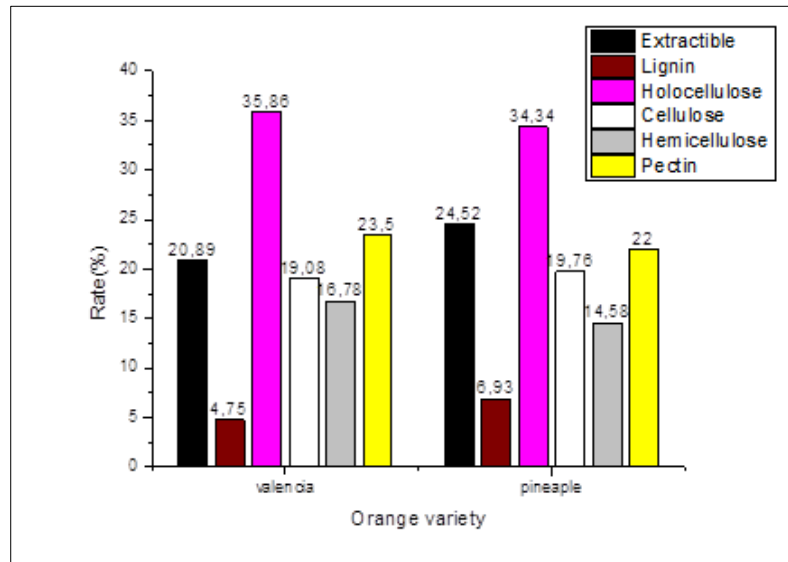


Figure 5 Fiber contents

4. Conclusion

This study has highlighted the lignocellulosic properties of the peels of two varieties of orange. The results obtained show us that whatever the nature of the orange, their peels have very interesting physicochemical characteristics for their use in the formulation of biodegradable plastic films. The fiber contents obtained justify the use of orange peels in the production of biodegradable plastic films.

Indeed, the formulation of biodegradable plastic films from orange peels will not only allow us to obtain a product with high added value but also to clean up our environment. Our future work will focus on the formulation of biodegradable plastic films using the characterized orange peels.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

The authors agree no conflict of interest.

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