The Pharmaceutical and Chemical Journal, **2016, 3(2):143-148**

Available online www.tpcj.org

Research Article

ISSN: 2349-7092
CODEN(USA): PCJHBA

Valuation of Dates Cores of the Southern Region of Morocco (Zagora): Isolation of Hemicellulose and Their Use in the Development of Biodegradable and Hydrophobic Film

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Abstract The nuclei of dates, from domestic consumption or as waste from the agro-food sector (date tab, syrup, oi etc.) on a small or large scale, or simply contained in the inedible dates, which remain abandoned in palm trees, are a very interesting material for the production of high value added products. They consist mainly of plant cell walls (cellulose, hemicellulose and lignin) that represent 82% to 92% of the initial dried material. The purpose of this study is the extraction of hemicellulose from the nuclei of dates first, then their introduction with the starch in the development of biodegradable and hydrophobic films. Hemicellulose in the nuclei of dates consist in large part of mannane. The originality of the method of extraction of the hemicelluloses in our study, is the first time use of calcium chloride instead of zinc chloride widely used in the presence of acetic acid. Those fresh conditions allow the simultaneous obtaining of lignin and hemicelluloses, making the process economically interesting.
The film preparation is carried out from a mixture containing corn starch, glycerol, a hydrochloric, an acid solution and a sodium hydroxide solution. Different fractions of hemicellulose derived from the nuclei of dates are added to this mixture with percentages going from 5% to 20% by weight compared to the starch.
Hemicelluloses cores dates are constituted in large part by mannan, which are insoluble in water (ref book and article). Their introduction in the development of films has the consequence of reducing their water sensitivity.
To confirm the biodegradability and hydrophobicity of these films, we have conducted tests such as the measurement of moisture absorption, of water absorption and of weight loss of films.

Keywords G. Senegalensis, Wistar Strain Albino rats, alanine amino transferase, aspartate amino transferase, total protein, urea, creatinine, packed cell volume and hemoglobin.

Introduction

The date cores are residues obtained in large quantities by the agro-food sector (date tab, syrup, oil etc.). The production of dates in Morocco is estimated at nearly one hundred thousand tons per year. Half of this production consists of low range; the value date is not as competitive [1-2]. Much is used as animal feed [3], when it could be valued in an appropriate transformation as biodegradable packaging. In recent years, an increasing trend was observed towards the use of agro-industrial residues as raw materials for the materials industry. In fact, the extensive use of synthetic packaging films has led to serious environmental problems because of their total non-biodegradability.
The food packaging industry, concerned about the protection of all types of foods and their raw materials against oxidation and microbial contamination, and also the protection of their characteristics during the retention period, is interested in increasing substitution of synthetic packaging films with those from renewable resources, respectful of the quality of food and the environment.
One of the most interesting solutions for the packaging industry is the development of biopolymers from renewable resources, with many thermoplastic and biodegradable properties, could replace synthetic polymers. Several studies mention the use of starch because of its availability at a competitive price. However many works which he was the subject [4-5] show that once soaked in liquid, starch has relatively poor mechanical properties and the need to

associate with this hydrophilic polymer another hydrophobic reinforcement to maintain the mechanical strength of the product is important.

Our study is to develop a new method of extracting hemicelluloses from the nuclei of dates and integrate them in the development of the films based on starch.

Hemicelluloses dates cores consist largely of mannane, insoluble polysaccharides in water [2]. Indeed, in this work we seek to exploit this feature by introducing these hemicelluloses in developing films based on starch, in order to improve their properties and make them less sensitive to water. The extraction of hemicelluloses from plant substrates has been the subject of numerous studies. In general, this extraction is carried out by alkaline solutions [6-7] or acid [8-10].

In this work, we have adopted new extraction conditions of hemicelluloses from dates cores, which consists of replacing the zinc chloride widely used by calcium chloride in the presence of acetic acid.

The film preparation is made from an initial mixture formed by starch and hemicelluloses, whose percentages vary from 5% to 20% relative to the starch.

Method

The nuclei of dates used are from the southern region of Morocco (Zagora).

Samples cores dates are washed, dried, and frozen at a temperature below 4 °C to facilitate grinding.

Pre-treatments of the plant material

The great structural diversity of plant cell walls, from which the hemicelluloses are extracted, first requires various treatments to improve the extraction of these polysaccharides. Although some of these polysaccharides is removed or degraded during these pre-treatments, whether physical or chemical, they are designed to eliminate certain non-desirable molecules (proteins, tannins etc).

Oil extraction

This step is to remove and extract the oils and fats.

In a cellulose cartridge, we introduced 130 g of dried and ground plant material. The cartridge is placed in the Soxhlet extractor, connected to a one-liter flask, containing 400 ml of hexane. The extraction is maintained for 6 hours.

Ethanol extraction

This step allows the elimination of free sugars (glucose, fructose, sucrose etc) and a large part of the tannins. The sample is heated to 60 °C with stirring for 3 hours in 500 ml of ethanol. After filtration, the residue obtained is dried in an oven at 40 °C for 5 hours.

Extraction with hot water

This step removes the majority of the pectins. The residue extracted with ethanol is dried and put into a flask containing a volume of 400 ml of distilled water and then heated in a water bath with mechanical stirring at a temperature of 100 °C for 4 hours. The residue obtained is filtered and then dried in an oven at 40 °C.

Extraction of hemicellulose

Procedure

In a 250 ml flask are introduced, the resulting residue, a solution of acetic acid, water and calcium chloride.

The reaction mixture is refluxed in a water bath at a temperature between 75-80 °C with stirring for 3 hours, then cooled and filtered under vacuum.

The filtrate, which consists of a mixture of lignin and hemicelluloses is concentrated in a rotary evaporator under reduced pressure. Hemicelluloses are precipitated by the addition of ethanol. Hemicelluloses obtained were dried at 40 °C. The yield of hemicelluloses is in the range of 20% relative to the dry matter. This low yield may probably be the cleavage of some glucoside bonds sensitive to acid, as it was reported in the literature [11].

Development of films

In a beaker was formed, by heating a mixture, the corn starch, glycerol (in a ratio of 60%: 40%), a solution of hydrochloric acid, water (3 ml of a solution of hydrochloric acid 0.1 mol / l, in 70 ml of water to 5 g of starch) and a variable amount of hemicellulose from 5% to 20%, relative to the starch. The mixture was stirred for 15 min at 100 °C until obtaining a homogeneous medium. After neutralization with a sodium hydroxide solution, the mixture is spread on a glass plate with a thickness of about 4 mm and allowed to dry in open air. The films obtained are homogeneous and have a plastic appearance (Figure 1).

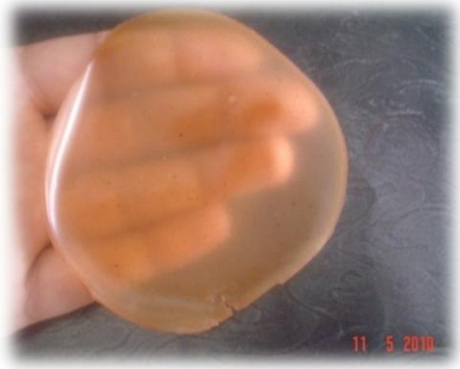


Figure 1: Image of a starch film reinforced by 20% hemicellulose dates cores

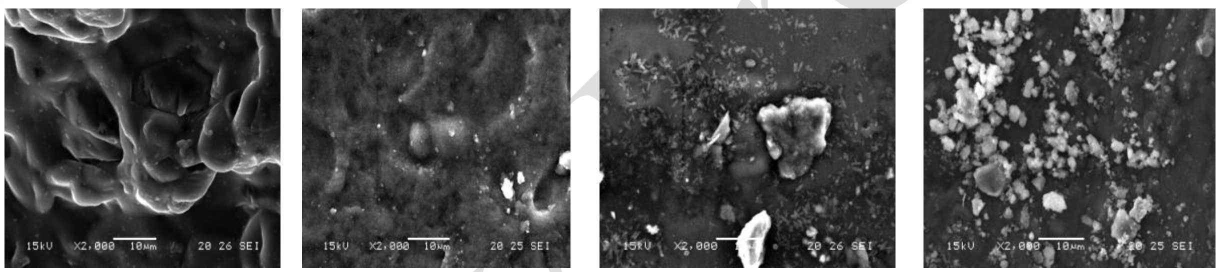
Characterization of the films

In this study, we focused especially on hydrophobic and biodegradable film characters.

Methods and Discussions

Scanning Electron Microscopy

The surfaces of the individual films are scanned by electronic scanning microscopy (SEM). The images obtained showed the presence of new elements dispersed on their surfaces, which can be attributed to the hemicelluloses. (Fig. 2).



(a) (b) (c) (d)

Figure 2: Scanning electron microscopy of the starch film reinforced by hemicelluloses cores dates:
(a) 0% hemicelluloses, (b) 10% of hemicelluloses (c) 15% of hemicelluloses, (d) 20% of hemicelluloses

Study of the water sensitivity of the developed films. To determine the water sensitivity of the films obtained, we measured their moisture and water absorption.

Measurement of moisture absorption (Hygroscopicity)

Hygroscopicity was determined by monitoring the evolution of the mass of individual films, placed in a desiccator, packed in an atmosphere of 75% with a saturated NaCl solution. After drying at 45 °C for 48 h, the samples were weighed and placed in the desiccator. They were then removed regularly from the chamber, weighed and placed again in the desiccator. Mass measurements were performed until saturation of the film to water vapor. Moisture absorption is calculated using the formula:

$$\text{Moisture absorption} = \frac{m_2 - m_1}{m_1} * 100$$

With: m_1: initial mass film and m_2: mass after moisture absorption.

The percentages of moisture absorption are given in Table 1.

Table 1: Moisture absorption measurement samples of the starch film reinforced hemicelluloses extracted from nuclei of dates.

Nature of sample	Moisture absorption (%)
Starch	36 ,01
Starch + 5% hemicelluloses	13,24
Starch + 10% hemicelluloses	9,50
Starch +15% hemicelluloses	8,21
Starch + 20% hemicelluloses	7,17

We find, from Table 1, the value of moisture absorption decreases with increase in the fraction of the hemicelluloses in the developed films.

Measurement of water absorption

To monitor the absorption of water by the films, we used gravimetry. It is to follow the mass development of samples over time, measured at regular intervals.

Films were dried in an oven at 70 °C until constant weight, weighed and then placed in a bath of distilled water. At the time of the mass measurement, the samples were removed from the bath, lightly wiped off with a paper towel, weighed and re-immersed in the bath

Water absorption is defined by the following formula:

$$\text{Water absorption (\%)} = \frac{m_2 - m_1}{m_1} * 100$$

With mass m_1 original film and mass m_2 after water absorption.

The figure 1 shows the evolution over time of water absorption by the various films.

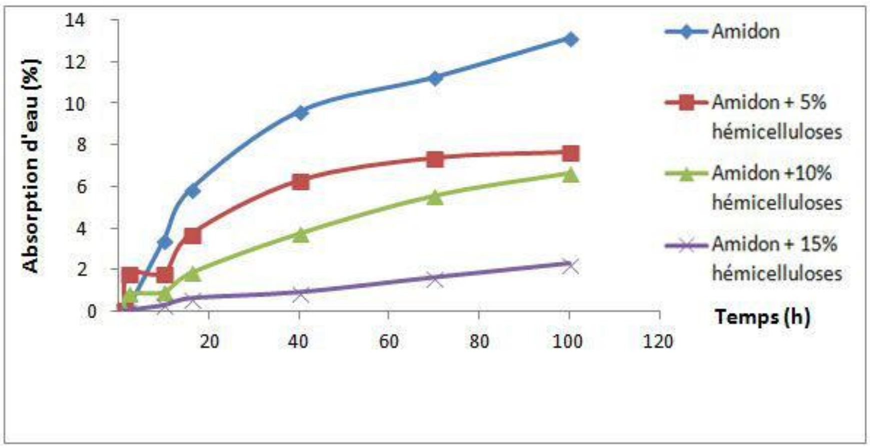
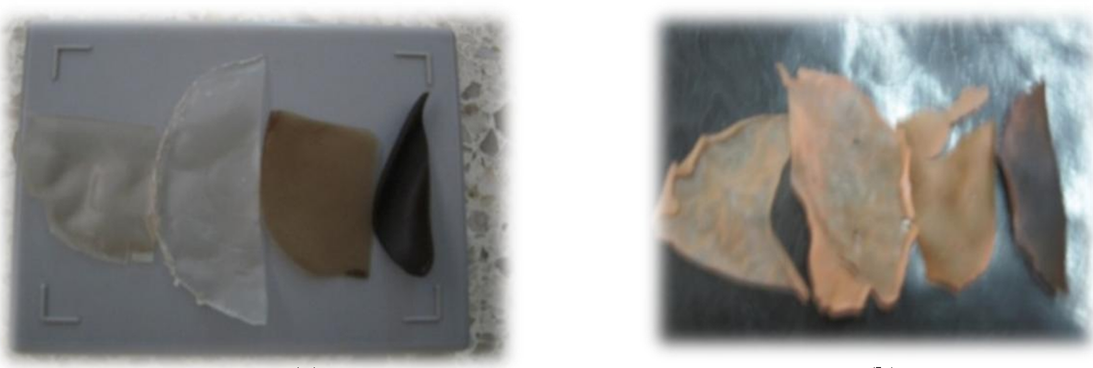


Figure 1: The evolution over time of the water absorption by the starch-based films according to different fractions of hemicellulose.

We find that the more you increase the fraction of hemicellulose in films, the more the change in their mass decreases and consequently, their water absorption.

The biodegradability

The biodegradability was evaluated by measuring the weight loss and the deterioration of the film surface. The individual films were dried in an oven at 70 °C until constant weight, photographed, and then placed in natural soil (60% moisture) at a depth of 8 cm. Samples were withdrawn regularly from the ground, weighed and placed back into the ground. After 25 days, they were removed from the soil, photographed and weighed. Figures 5 and 6 show on the one hand, a degradation of the surface of the individual films and secondly, a slight loss of weight.



(a) **(b)**

Figure 5: Surface different films before (a) and after 25 days of treatment in the soil (b).

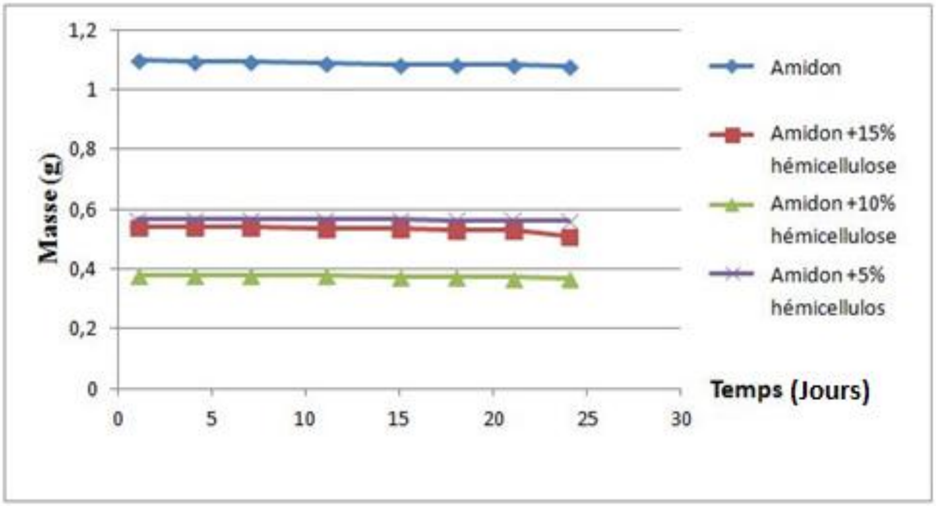


Figure 6: Evolution of mass loss over time for various films based on starch and hemicellulose nuclei of dates, placed for 25 days in soil.

In the native state, starch has a temperature melting point higher than its degradation temperature, phenomenon related to the density of intermolecular hydrogen interactions. For use in plastics, it is necessary to transform the thermoplastic starch [12]. This transformation is achieved through the incorporation of plasticizers which will cause the destruction of the crystalline structure of starch. The plasticizer is inserted by diffusion between the starch chains to break the hydrogen bonds inter-chain starch and create new hydrogenated starch-plasticizer links. Breaking intermolecular bonds increases the mobility of the chains and reduces the melting temperature of the starch. Different plasticizers were used, the more used is glycerol, but studies have shown that materials from starch and glycerol are sensitive to water even at 25 °C [12, 13, 14]. This result is confirmed in our case by the moisture absorption measurements and water uptake measurements. However, in the presence of hemicellulose from the nuclei of dates, the same tests showed an improvement in hydrophobicity of the films in a very clear manner. This is due to the fact that the hemicelluloses cores dates are constituted largely by mannans. These are insoluble in water [2], act by decreasing the sensitivity of the films to water.

The degradation of the surface of the films placed in the ground at a depth of 8cm, while nearby month and the measurements obtained after each weighed, show that there is a slight loss of mass, which confirms their biodegradability.

Conclusion

In this study, we extract hemicelluloses from the nuclei of dates, from a region in southern Morocco (Zagora), with an original method using acetic acid, calcium chloride and water. The extracted hemicellulose were subsequently used with the starch in the development of films. Tests such as, determining the extent of moisture absorption, measurement of the water absorption and the biodegradability tests have shown that these films have the potential to give interesting hydrophobic and biodegradable materials for the sector of food industry.

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