

Euro Polymer Science-2020 Characterization of components isolated from algerian apricot shells (*prunus armeniaca l.*) - Djennat Allouch, University Chadli Bendjedid El Tarf

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Shells resulting from food processing and agricultural activities, such as hard shells of apricot, are considered as wastes and are generally used as fuel. However, this residue shows promise as lignocellulosic feedstock for biorefineries, for its conversion to liquid fuel or bio-products. This study is dedicated to the characterization and isolation of lignin, cellulose and hemicelluloses from apricot shells (AS). The chemical composition and thermal stability of AS after chemical treatment with solvents (ethanol-toluene), cellulose, hemicelluloses and lignin were analyzed by standard methods, i.e. Fourier-transform infrared spectroscopy (FTIR) and thermo gravimetric analysis (TGA). Further, almost 50.2 wt% of a water-insoluble extract was obtained after the bleaching process, which showed the removal of lignin, and the final percentages for this extraction were $50.2 \pm 0.34\%$, $26.5 \pm 0.83\%$, $23.7 \pm 0.29\%$ and $35 \pm 1\%$ for holocellulose, cellulose, hemicelluloses and lignin, respectively. FTIR spectroscopy evidenced the structure of lignin, cellulose and hemicelluloses. Thermal analysis and the kinetic study suggested that cellulose had higher thermal stability than the other components, with the activation energy of 289.62 kJ/mol. Thus, our results indicated the high potential of AS to be used as an environmentally friendly material in a biorefinery, as well as in the modern polymer and chemical industries.

INTRODUCTION:

The rapid increase in agricultural wastes is one of the major environmental concerns, since the disposal of these wastes on the soil or in landfills causes serious environmental problems. This problem has turned the researchers' attention towards the valorization of agricultural residues,

as well as towards the development of recyclable or biodegradable products.^{1,2} Thus, the generation of lignocellulosic residues as agro-industrial by-products poses a challenge from the point of view of environmental protection, as well as for the progress of a "green" economy.³⁻⁵ Lignocellulosics are the most abundant source of insufficiently exploited biomass on the earth.

They mainly consist of three polymers: cellulose, hemicelluloses and lignin, representing the three main constituents of the cell walls of plants, in which they are not uniformly dispersed. The structure and quantity of these plant cell wall components vary according to the species, tissues and harvesting period.² In general, lignocellulosic biomass is composed of 40-50% cellulose, 25-30% hemicelluloses and 15-20% lignin, as well as a small amount of other extractives.⁶ *Prunus armeniaca L.* is classified under the *Prunus* species of the *Prunoidae* sub-family and the *Rosacea* family. At present, the apricot is cultivated in a diverse area with suitable climates.

EXPERIMENTAL

Materials and methods Raw materials, chemicals and pretreatment methods Apricot fruits (*P. armeniaca L.*) were collected from the Menna region, located in Batna in the North East of Algeria. The apricot shells obtained were dried at room temperature during several days, ground by an electric mixer to a fine powder and sieved over a 20-80 mesh screen to maintain the size uniformity of powdered shells, as per previous National Renewable Energy Laboratory NREL standard methods. The dry powder of AS (20 g) was extracted with a 2:1 v/v ethanol/toluene (300 mL) mixture for 8 h to remove phenolics, pigments, wax and oils, followed by oven-drying at 50 °C for 24 h. The

treated powder was used to find out the content of holocellulose, cellulose, hemicelluloses and lignin, and was stored at 4 °C for further analysis. The chemicals used in the present study were the following: potassium hydroxide (>97%) purchased from Merck KGaA Company, Germany; sodium hydroxide (>99%) from Merck KGaA Company; nitric acid (>65%) from Chemical Company, Iasi; acetone (>99.8%) from Chemical Company; sulfuric acid (>96%) from Sigma–Aldrich; sodium chlorite (>25%, Synth) from Merck KGaA Company; glacial acetic acid (>99.8%) from Chemical Company, Iasi; ethanol (99.5%, Synth) from Chemical Company, Iasi; toluene (>99%) from Chemical Company, Iasi; hexane (>99.8%) from Chemical Company, Iasi.

Physico-chemical composition

The chemical composition, moisture (%) and ash (%) content of the apricot shells were determined according to the standard methods of NREL, with the exception of holocellulose, which was determined by the sodium chlorite method. The average of three replicates was calculated for each sample.

Isolation of acid insoluble lignin

An amount of AS extracted powder of 1 g was mechanically stirred in 15 mL of 72% H₂SO₄ (v/v) aqueous solution at 25 °C, in the powder/solution ratio of 1:15 (g/mL), for 2.5 h. The suspension was subsequently diluted with 200 mL of distilled water and heated at 90 °C for 1 h. Then, it was filtered on a sintered glass crucible G3 filter and washed with hot distilled water until neutral pH was reached. Finally, drying was carried out in an oven at 105 °C until constant mass was reached.

Isolation of cellulose and hemicelluloses

Separation of holocellulose An amount of 5 g of extracted powder was mixed with 150 mL of distilled water, in the presence of 1.5 g of sodium chlorite and 10 drops of glacial acetic acid, for one

hour at the temperature of 80 °C, under mechanical stirring. After 1 h, 1.5 g of NaClO₂ and 10 drops of glacial acetic acid were added to the mixture. The reaction was continued for 1 h and was repeated for 4 times. After the treatment, the holocellulose suspension was cooled in an ice bath, filtered on a sintered glass crucible G2 filter, washed with distilled water to neutral pH and then with acetone, and finally, was oven dried at 50 °C to constant mass.

Separation of hemicelluloses

An amount of 1 g of holocellulose was treated with 25 mL of potassium hydroxide (15%) for 2 hours at room temperature (25 °C). It was then filtered on a sintered glass crucible G2 filter, and the solid bleached phase obtained was cellulose, while the liquid fraction represented the hemicelluloses content. The liquid fraction was acidified with acetic acid to pH 5-6 and then precipitated in 5 volumes of ethanol. The residue obtained was filtered through a sintered glass crucible G2 filter, washed with ethanol and finally oven dried at 50 °C to constant weight.

CONCLUSION

This work reports on the extraction of the main components of apricot shell biomass. FTIR spectroscopy and TGA have been used to characterize them. The removal of lignin has been confirmed by the absence of the peaks at 1502, 1508 and 1612 cm⁻¹ in the FTIR spectra, suggesting the great efficiency of the bleaching process. TGA revealed that the cellulose extracted from the apricot shells has good thermal stability, followed by lignin, treated AS and hemicelluloses. The analysis of the FTIR spectra evidenced the structure of cellulose, hemicelluloses and lignin, which confirmed that apricot shells (AS) are a lignocellulosic biomass source with relatively high cellulose, hemicelluloses and lignin contents. This makes apricot shells (AS) an interesting and

advantageous material for various valorization methods.