UTILISATION OF *ASTRAGALUS ARMATUS* ROOTS IN PAPERMAKING

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The chemical composition of *Astragalus armatus* contains quite a high amount of extractives in organic solvents (close to 13%), but a low percentage of lignin (around 17%) and an acceptable content of holocellulose (54%). The α-cellulose content is around 35%, and the ash content is around 3%. Using the insight of such data, the soda-anthraquinone cooking of *Astragalus armatus* produced lignocellulosic fibres. Different cooking temperatures (100, 120, 140, and 160°C) were tested and the delignification duration was 2 h. A yield of about 30% w/w was obtained, and the obtained pulps had a kappa number of 25. Finally, the isolated fibres were used to produce paper samples with a basis weight of 60 g/m^2. The structural and mechanical properties of the prepared samples were close to those of other common annual plant-based fibre mats.

Keywords: Astragalus armatus; Fibre properties; Annual plant; Paper properties; Pulping process

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INTRODUCTION

Wood is the most widely used raw material for the production of pulp and paper (Edgrard 1999; Khristova et al. 1997; Fidel et al. 2003; Jahan et al. 2008a,b; Malinen et al. 2006; Zhu et al. 2005). In fact, paper consumption is continuously increasing across the world, and the available wood supply will not meet the growing demand (Jahan et al. 2007; Hurter et al. 1998). A part of this increase in fiber demand will be met by increased forestry production, which will give rise to global deforestation, with harmful results to the environment (Cordeiro et al. 2004). However, the increasing fiber concerns and the potential increases in wood costs have caused the pulp and paper industry to search for alternative fiber sources from a variety of annual plants and non-wood fiber plants. Many studies have been carried out to evaluate some fast-growing species for use in the pulp and paper industry (Edgrard 1999; Khristova et al. 1997; Fidel et al. 2003; Jahan et al. 2004, 2008a; Malinen et al. 2006; Zhu et al. 2005; Lei et al. 2006). Fidel and Tamayo (Fidel et al. 2003) determined the chemical composition of *Acacia mangium*, and the results showed that this plant can be used for pulp wood and paper production. The Nalita wood (*Trema orientalis*) and Pati (*Typha*) are native species grown in tropical and temperate regions. Jahan et al. introduced these species as a pulping raw material for papermaking (Jahan et al. 2004, 2007, 2008b, 2010). A study carried by Wanrosli et al. (2007) showed that pulp from oil palm fronds might be used as a reinforcement pulp in mechanical grade pulps such as newsprint. Oliveira et al. (2002) have started research studying the chemical and structural constitution of banana plants and the use of their cellulosic fibres in papermaking. The authors proved several advantages, one of which is that the resulting pulp can be used in paper and board (Oliveira et al. 2002).

Astragalus armatus, chamaephyte of the family of Leguminosae, constitutes a significant element of the North African vegetation (Tunisia, Morocco, Algeria). This plant is adapted to the severe climatic conditions of edaphic poverty. It presents a good germinative aptitude in the natural environment with its rooting able to develop in the weak hydrous reserves of the ground. This work aims at the valorization of *Astragalus armatus* in the manufacture of paper.

EXPERIMENTAL

Material and Chemical Analysis

Roots of *Astragalus armatus* were collected from the region of Gafsa, Tunisia. The chemical composition was determined in accordance with TAPPI Standard T264 om-88. Water extractives (T207 cm08), 1% alkali solubility (T212 om07), extractives (T204 om07), Klason lignin (T222 om08), and ash content (T211 cm07) were determined in accordance with TAPPI Test Methods. The cellulose content was determined following the Kurschner-Hoffner approach (Browning 1967). It consisted of treating 2 g of extractive-free samples with 50 mL of alcoholic nitric acid solutions under reflux during four cycles of 1 h. After each cycle, the alcoholic nitric acid solution was removed and a fresh volume was added. The alcoholic nitric acid solution consisted of mixing one volume of 65% (w/w) solution of nitric acid with four volumes of 96% purity ethanol. At the end of the four cycles, the cellulose was washed, dried and weighed. Holocelluloses were determined according to the method described by Wise et al. (1946).

Elemental analysis was determined from XPS spectra. The X-ray photoelectron spectroscopy (XPS) experiments were performed with a XR3E2 apparatus (Vacuum Generators, UK) equipped with a monochromated Mg Kα X-ray source (1253.6 eV) and operating at 15 kV under a current of 20 mA.

Pulping

To optimise the cooking conditions, chips of *Astragalus armatus* roots were prepared and put on rotational thermostated digesters having a volume of 1 L (60 g of oven-dried material, 0.1% of anthraquinone, and liquor/crops ratio = 1/10) controlled by an ES100P apparatus. The effects of temperature (100, 120, 140, and 160°C), the sodium hydroxide concentration (5, 10, and 15%), and times at constant temperature (30, 60, and 120 min) were studied. After cooking, the cooked material was separated from the black liquor, disintegrated, screened, and washed with copious fresh water. The disintegrator enabled pulp screening, which allowed the determination of both the total pulp yields and the screening rejects by weighing each fraction after drying. The residual lignin in the pulps was assessed by determining the kappa number. The kappa number was determined using TAPPI Method T236 om06, and the degree of polymerisation was calculated from viscosity data (T230 om99).

Pulp yield was calculated as the ratio of the weight of obtained material after washing to that of initial raw material.

Morphological properties of the fibres were studied by SEM observations and by using a MORFI analyzer. The main fibre parameters were assessed by image analysis of a diluted suspension flowing in a transparent flat channel observed by a CCD video-camera.

Evaluation of Pulps

Pulps were disintegrated in a standard disintegrator. The sheets were made in a Rapid Kothen Sheet Making Machine according to Standard Method ISO5269. The sheets were tested for tensile, burst, and tear strength according to TAPPI Standard Test Methods.

RESULTS AND DISCUSSION

Chemical-Physical Properties

The results obtained (Tables 1 and 2) showed that the roots of *Astragalus armatus* had three major components: cellulose, extractives, and hemicelluloses. The remainder of the composition included lignin and mineral matter.

The extractive contents, including those from hot and cold water, were higher in the roots of *Astragalus armatus* than in *Trema orientalis* (Jahan et al. 2010), pati (Jahan et al. 2007), other wood and non-wood sources (Copur et al. 2008; Jimenez et al. 2008; Eugenio et al. 2006), and other grasses (Radiotis et al. 1999). The extractive contents are comparable to some annual plants such as Jerusalem artichoke and amaranth (Fiserova et al. 2006). The high solubility in 1% NaOH (32.7%), indicated easy access and degradation of the cell wall material by weak alkali. The Klason lignin in *Astragalus armatus* roots was low, compared to wood (Goyal et al. 1999). Easier pulping in an alkaline medium was also expected because of their lower lignin content. The holocellulose (54%) and the cellulose (35%) content were lower than wood and non-wood sources (Copur et al. 2008; Jimenez et al. 2008; Eugenio et al. 2006), but comparable to some annual plants (Fiserova et al. 2006; Alcaide et al. 1990). Both values would be reasonable if one took into account the high extractive components, which would lead to promising perspectives concerning the valorization of roots of *Astragalus armatus* for papermaking in the current study.

The bands at 3342, 2928, 1730, 1632 and 1028 cm^{-1} are associated, respectively, with the stretching vibrations of the OH, C-H, C=O, C=C, and C-O groups (Table 2). A broad shape of the C=O peak indicated that it had established hydrogen bonds with the hydroxyl groups.

The elemental analysis (Table 3) showed high proportions of silicon, calcium, and potassium, but small proportions of carbon, magnesium, and sodium. The proportions of iron, sulfur, copper, and phosphorus were negligible.

Table 1. Chemical Composition of *Astragalus armatus* Roots

Extractive (%)	cold water	26.2
	hot water	33
	1% alkali (NaOH)	32.7
	ethanol-toluene	13
Ash (%)		3
Klason lignin (%)		16.75
α-cellulose (%)		35
Holocellulose (%)		54

Table 2. IR Spectrum

Frequency (cm^{-1})	
3342	ν OH
2928	ν C-H
1730 (broad shape)	ν C=O
1632	δ OH, ν C=C
1422-1370	δ CH2
1028	ν C-O
566	δ C-H

ν : valence vibration; δ : deformation vibration.

Table 3. Elemental Analysis

C	4.1 %
S	0.94 %
Si	18.42 %
Ca	11 %
Mg	2.98 %
Fe	0.29 %
Cu	$<$ 0.1 %
K	8.11 %
P	0.59 %
Na	1.8 %

Morphological Properties

The images obtained by a scanning electron microscope showed that the roots of *Astragalus armatus* (Fig. 1) present several porous fibres with the presence of some minerals fixed on wood and bast fibres and vessels. The presence of these crystallized minerals confirmed the conducting function of fibres and the vessels.

The Optimisation of Pulping Process

Before producing pulp from the roots of *Astragalus armatus* and to avoid extensive consumption of raw material, delignification was carried out to provide suitable pulps to be investigated in terms of kappa number and pulp yield.

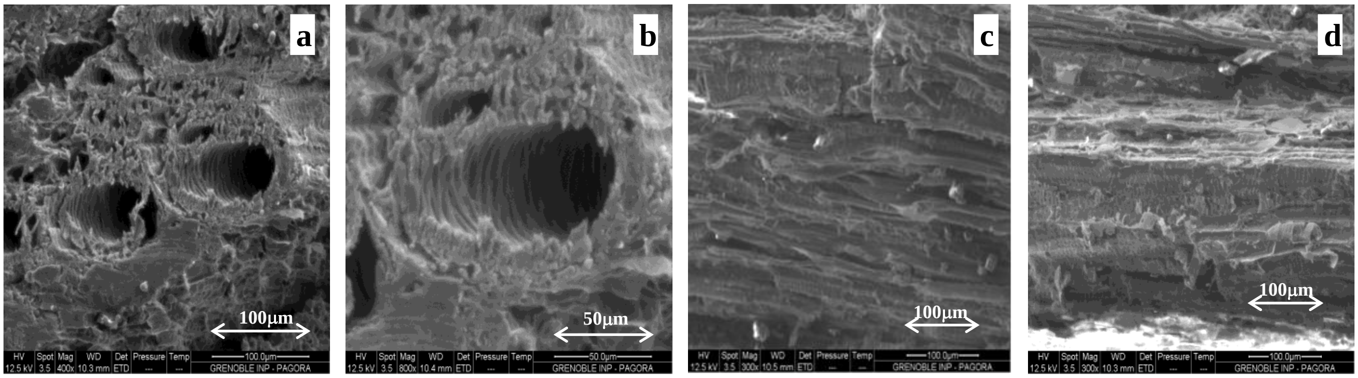

Figure 1. SEM images of roots of *Astragalus armatus* (a and b: transverse section; c and d: longitudinal section)

The influence of temperature

When the temperature was increased from 100°C to 160°C, kappa number and pulp yield decreased (Fig. 2). The kappa number gives an indication of the delignification rate and degree of residual lignin of the pulp. At higher kappa numbers, there are many shives in the pulp. However, conditions that result in low kappa numbers should be adapted. With delignification at 140°C and 160°C, the kappa number was respectively 18.8 and 10.1. However, the pulp yield at 140°C was higher than the yield of delignification at 160°C (Fig. 2).

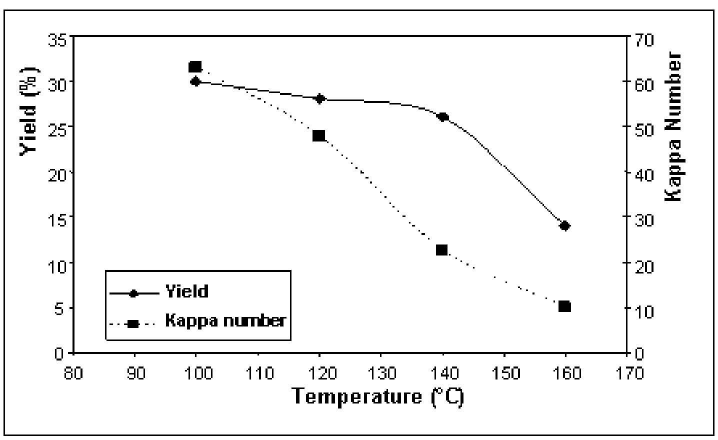

Figure 2. Effect of temperature on pulp yield and kappa number. (Cooking conditions: 60g of material, 15% of NaOH, 0.1% of anthraquinone, liquor/crops ratio = 1/10, 120 min of heating, temperature: 100, 120, 140, and 160°C), pulp yields were determined based on the weight of material initially charged to the digester.

The influence of time

The kinetics of delignification of *Astragalus armatus* roots were also studied at 140°C and 160°C (Fig. 3). As shown, the kappa number decreased with increasing time with a weak diminution of pulp yield at 140°C, and the pulp yield decreased to 14% if the time increased from 60 min to 120 min, but a weak decrease of kappa number was evident at 160°C. From the data it can be deduced that cooking should be done at a temperature of 140°C for 120 minutes.

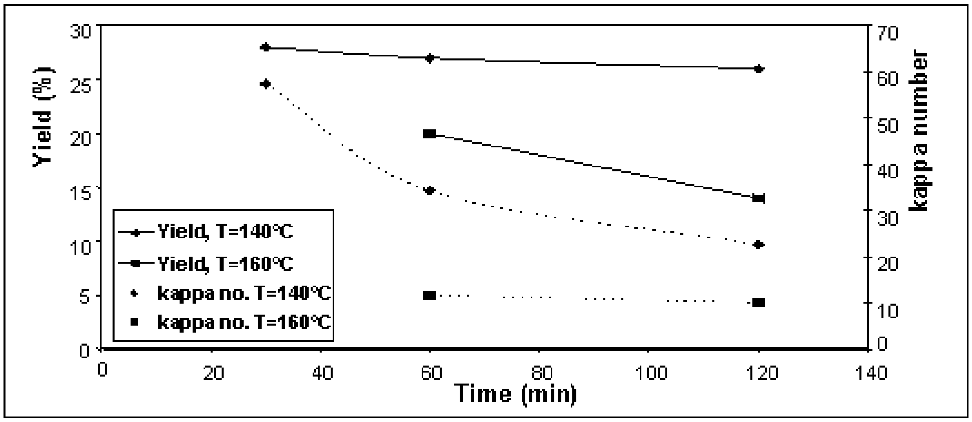

Figure 3. Screened pulp yields and kappa number as a function of cooking times for roots of *Astragalus armatus*. (Cooking conditions: 60g of material, 15% of NaOH, 0.1% of anthraquinone, liquor/crops ratio = 1/10, cooking time: 30, 60, and 120 min, temperature: 140 and 160°C)

The influence of sodium hydroxide concentration

The concentration of sodium hydroxide was varied from 5 to 15%. The obtained pulp yield, kappa number, and the degree of polymerisation are summarised in Table 4. The increase in the sodium hydroxide concentration produced a decrease in the screened pulp yield from 30 to 25.6% and a decrease of the polymerisation degree. Consequently, it induced carbohydrate degradation. This proved that the most favourable delignification occurred at 5% of sodium hydroxide.

Table 4. Kappa Number, Pulp Yield, and Degree of Polymerization as a Function of Sodium Hydroxide Concentration

Sodium hydroxide concentration (%)	5	10	15
Pulp yield (%)	30	25.6	26
kappa number	25.0	22.6	18.8
degree of polymerization	1629	1591	1137

(Cooking conditions: 60g of material, 5, 10, and 15% of NaOH, 0.1% of anthraquinone, liquor/crops ratio = 1/10, 120 min of heating, temperature: 140°C), pulp yields were determined based on the weight of material initially charged to the digester.

Pulp Characterization

The fiber dimensions of unbleached pulp from *Astragalus armatus* roots were determined in an unbeaten state (Table 5). The fibre dimensions of the obtained pulp slightly decreased with increasing sodium hydroxide concentration. Fibres had higher length and width values, compared to *Eucalyptus* and *Cynara cardunculus* globules (Abrantes et al. 2007). These fibre characteristics would probably influence the mechanical properties of the resulting paper. However, the cationic demand increased with increasing sodium hydroxide. Consequently, the proportion of lignin decrease and the elimination of undesirable elements became difficult. Results indicated that cooking with 5% NaOH at 140°C for 120 min can result in pulps with better quality. These suggestions were confirmed by SEM images of the different pulps (Fig. 4). As shown in the figure, the fibres of pulp obtained by cooking with 5% NaOH were quite separate, and the quantity of shives was very low compared to the other obtained pulps.

Table 5. *Astragalus armatus* Root Pulp Properties

Sodium hydroxide concentration (%)	5	10	15
Morfi length (μm)	1101	1069	1013
Morfi diameter (μm)	26.2	25.5	25.1
Cationic demand	3.31	9.84	12.5
Fines content (%)	25.5	25.2	25

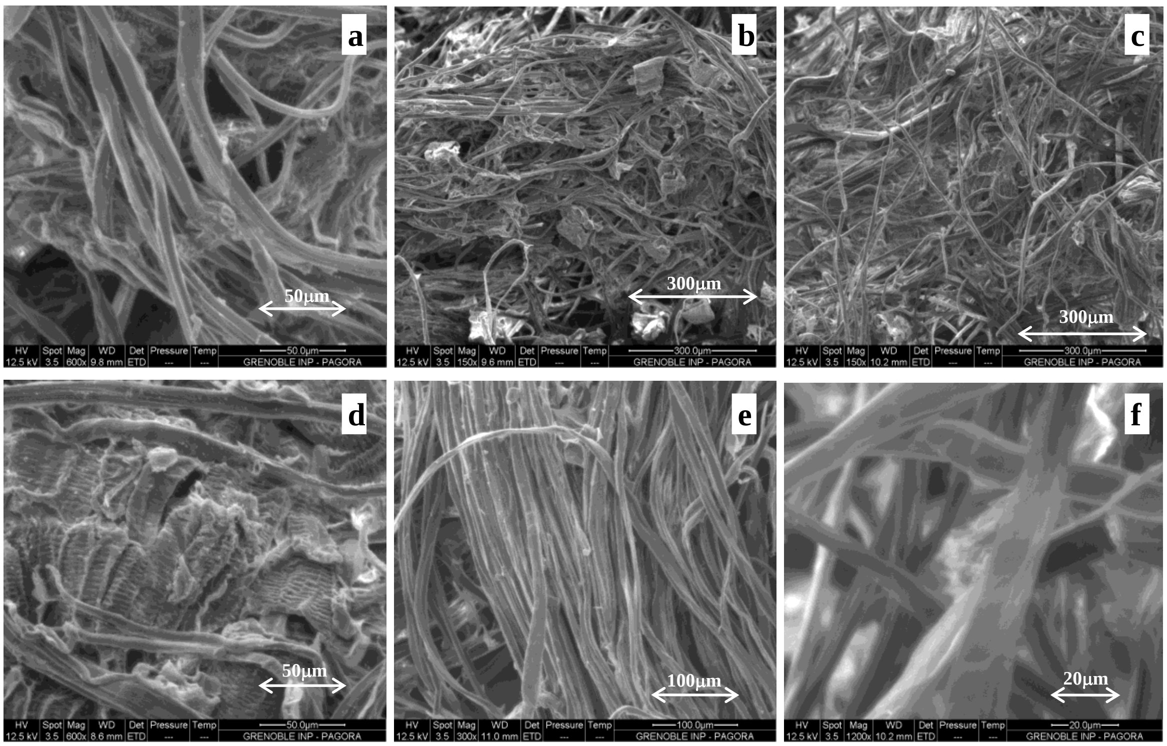

Figure 4. SEM images of *Astragalus armatus* roots pulp (a and b: 15% of NaOH; c and d: 10% of NaOH; e and f: 5% of NaOH)

Paper Characterisation

The paper was obtained from pulp at an 18°SR refining degree. SEM images (Fig. 5) showed the existence of accessory elements in the resulting paper. Density was higher for paper obtained from *Astragalus armatus* roots compared to *Cynara cardunculus L.* (pulp used has a 19°SR refining degree). This property resulted from an overestimated thickness of the sheet because of the fines content.

The low value for Young's modulus of the prepared paper (1.51 10^9 Pa) was attributed to the high value of the thickness (148 μm), which implies relatively low apparent density (Table 6).

All the mechanical properties of *Astragalus armatus* roots presented very good values for a non-refined pulp. This material could, thus, be regarded as promising for the purpose of papermaking.

Table 6. Comparison of Properties of Sheets Obtained from *Astragalus armatus* Roots and *Cynara cardunculus L*.

	Astragalus armatus	*Cynara cardunculus L.* (Antunes et al. 2003)
Basis weight (g/m^2)	58.2	61.4
Thickness (µm)	148.48±8.82	95.78
Bulk (g/cm^3)	2.57±0.15	1.56
Stretch (%)	2.17±0.43	2.8
Specific energy (mJ/g)	516.2±16.24	n.d
Young modulus (Pa. 10^9)	1.51±0.21	2.1
Burst index (KPa.m^2/g)	2.54±0.18	1.64
Tear index (mNm^2/g)	6.44±0.726	18.8
Internal resistance (J/m^2)	30.04±2.59	37.9
Breaking length (km)	3.31±0.70	3.32
Zero span breaking length (km)	9.53±0.86	7

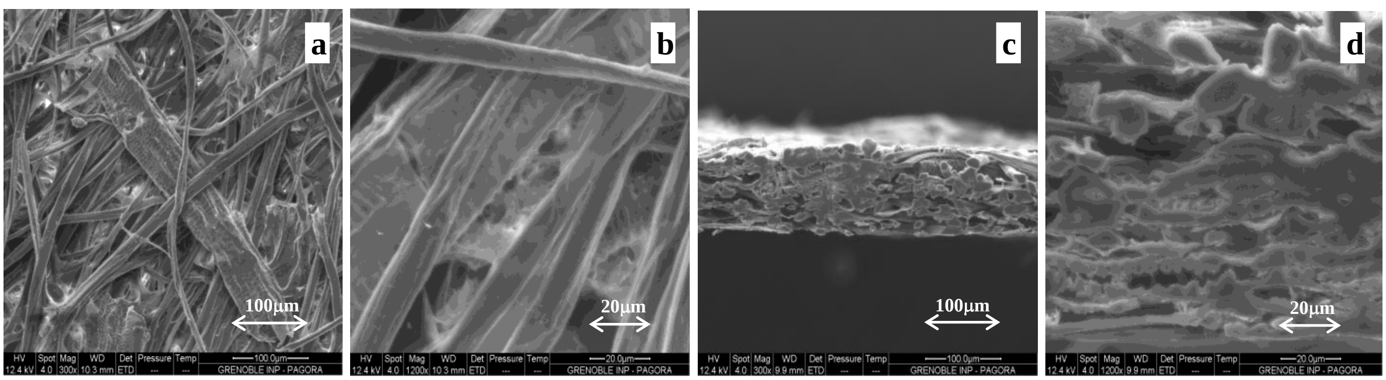

Figure 5. SEM images of *Astragalus armatus* roots sheet. (a and b: sheet surface, c and d: longitudinal section of sheet)

CONCLUSIONS

The objective of this study was to establish the suitability of *Astragalus armatus* roots as a source of lignocellulosic fibres for paper. The study confirmed the feasibility of paper sheets with a basis weight of 60 g/m^2 with good physical properties. Indeed, chemical characterization showed a low amount of ash and a high amount of extractives and holocellulose. In spite the low yield, the good pulping characteristics and high strength properties of *Astragalus armatus* roots are indicative that *Astragalus armatus* pulp can be suitable for production of paper that can be used in specific areas such as medicinal research. This feature can be considered as a serious advantage when looking for new alternative sources of fibres for papermaking. In fact, the use of Astragalus *armatus* as raw material for pulp and papermaking seems to be of great industrial importance because of its wide availability in the Saharan zones.

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