

## The Needles of Aleppo Pine From the Province of Taza-Morocco – A Biomaterial of Great Potential

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### ABSTRACT

The needles of the Aleppo pine (*Pinus halepensis*) (PA) are very abundant in the forest of the National Park of Tazekka (Ta-za-Morocco) and are unexploitable. Moreover, they constitute a potential danger because they facilitate the outbreak of wildfires. To solve this problem, we have considered turning these needles into a biomaterial that could be used as raw material for different uses, such as wastewater treatment. The biomaterial of the Aleppo pine is obtained from its needles which are harvested in spring, dried, cut, crushed, and sieved. The powder obtained is analyzed before and after the extraction of essential oil. The physicochemical and spectroscopic analyses show that this biomaterial is porous, hygroscopic, slightly acidic, moderately moist, and not very conductive. Its average density in the anhydrous state is 0.6. It is rich in carbon (79.91%) and oxygen (18.91%) in the form of aromatic compounds and ketone imprints; thus, relating the presence of cellulose, pectin, lignin, and hemicellulose. Its composition in mineral elements (Na, Mg, Ca, K, Cl, S) is deficient. Gas chromatography-mass spectrometry (GC-MS) analysis of the oils extracted from the needle powder relates that it is a complex mixture of bioactive compounds such as mono-terpenoid  $\alpha$  and  $\beta$ -pinene hydrocarbons. These results show that our biomaterial can be used as an adsorbent in wastewater treatment and the extracted essential oils can be used in the pharmacological, agro-food field.

**Keywords:** Aleppo pine needles; physicochemical and spectroscopic characterization; adsorbent; biomaterial; essential oil.

### INTRODUCTION

Biomaterials science is a constantly expanding area of research, encompassing a wide range of knowledge in different medical, industrial, and biological areas (Morris, Backeljau, and Chapelle 2019; Tamayo-Angorrilla et al. 2021; Deng et al. 2022). Due to many economic and environmental requirements, the industry is increasingly interested in the materials (Chegdani et al. 2017). Plant fiber reinforced materials are a current area of interest in composites research (Miraoui and Hassis 2012). It's involving the development of plastic products from lignocellulosic fiber

reinforced composites (Asyraf et al. 2022). Recent advances in natural fiber-based composites have minimized usage of synthetic fibers, which are detrimental to the environment due to their slow degradation, especially in structural applications such as aircraft stiffeners and rotor blades (Arumugam et al. 2022). We also mention the preparation of polysaccharide nanocomposites in the context of their potential use as food packaging materials, which have shown an antimicrobial effect that can provide food protection conditions (Pal et al. 2021). In general, composites with natural fiber reinforcements were high potential materials, offering many advantages over traditional

inorganic materials based on glass fibers or minerals, including lower cost, lower density, environmental impact, and many technical applications (Elouaer 2011). The reinforcing materials used as composite materials are diverse, such as particles and fibers, i.e., steel, aramid, carbon, glass, wood, and natural or cellulosic fibers. In recent years, the increasing global focus on energy consumption in the building sector has led to an interest in the use of materials of natural origin (Niyasom and Tangboriboon 2021) consisting of natural fibers from annual plants or agricultural or agro-industrial residues (Saad 2013). Indeed, the development of a biomaterial must consider its abundance and meet the pillars of sustainable development. In our case, we chose the needles of the Aleppo pine (*Pinus halepensis*) which grows in the park of Tazekka known for its floral diversity. Unfortunately, it is exposed to fires, especially in July and August. The senescence of Aleppo pine needles may increase the probability of crown fire development at the beginning of the fire season and could partly explain the concentration of fire activity in early July (Balaguer-Romano et al. 2020). To address this problem, we collected these needles and valorized them after performing a characterization to find possible uses for this material.

The Aleppo pine is a conifer of the genus *Pinus* belonging to the Pinaceae family. It is found mainly in North Africa and Spain (Najat Assem, Latifa El hafid, and Fatima Lamchouri 2018). It plays an ecological and economic role in low and medium-altitude Mediterranean regions. Furthermore, this species is well adapted to dry summer conditions and successfully colonizes abandoned arable land and burned areas (Deng et al. 2022).

In Morocco, Aleppo pine covers an area of 65,000 hectares, spread over the Mediterranean slope of the Rif, the central Middle Atlas, and some valleys of the High Atlas (Simón et al. 2021). At the level of the Middle Atlas southwest of the city of Taza -Fez-Meknes-Morocco Region, is located the Tazekka National Park (created in 1950) that hosts several floristic species

including the Aleppo pine. Indeed, the Tazekka pine is the most widespread and well-known resinous plant on the whole Mediterranean contour (Saad et al. 2014).

Several derivatives from the Aleppo pine are used as raw materials in different fields. For example, the resin is used to manufacture paints and rubbers, perfumes for cleaning products, pharmaceutical industry. Pine nuts are exploited in the culinary field, entering many Mediterranean recipes (Najat Assem, Latifa El hafid, and Fatima Lamchouri 2018). While the wood is of poor quality (abundance of knots, poor shape of the barrel, low natural durability, resin pocket, etc.), often used in the field of construction and as a source of energy by the local population. The latter use can be performed by pallets and pellets manufacturing (Elaieb et al. 2019). Moreover, pine sawdust and charcoal from pine sawdust, are used in the manufacture of porous clay bricks, characterized by their lightness (Simón et al. 2021). The bark of Aleppo pine is used in formulations of glues for wood (Saad et al. 2014). While the persistent needles of Aleppo pine are not yet exploited. In addition, active (AC-PW) and inactive (C-PW) carbonaceous materials are prepared from the fruit shell of Brazilian pine and used as adsorbents of dyes and some heavy metals from aqueous effluents (Calvete et al. 2010).

In this last field, several works have focused on the choice of an adsorbent that meets the criteria of efficiency, stability in the environment, regeneration, and low investment cost especially when it comes to the removal of heavy metals (Zhu et al. 2019; 2022). Our laboratory has tested several adsorbents based on natural materials such as the use of snail shells for the removal of copper from aqueous solutions and the production of valuable compounds (Ouafi, Asri, et al. 2021), the exploitation of powder from pinecones for the removal by adsorption of copper ions from water (Ouafi, Omor, et al. 2021) and the use of sawing for the treatment of heavy metals from contaminated wastewater (Ouafi et al. 2017).

To find integrative solutions to the risks of forest fires that could be triggered by Aleppo pine

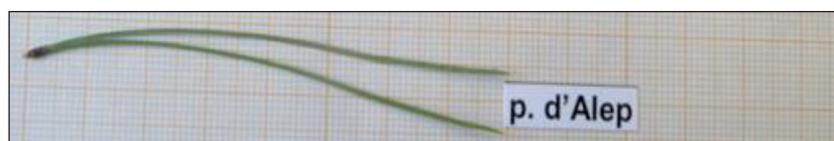


Figure 1. Aleppo pine needles

needles and because of our laboratory's work in the field of water treatment, we have chosen to characterize Aleppo pine needles (Fig. 1) to predict whether they can play the role of a biomaterial in this field.

The works on this biomaterial are very scarce, and the problem of the fires does not stop worsening, especially with the climatic change. Therefore, this work is an orientation of the interest of the local researchers toward this biomaterial. It's consisting of a physicochemical characteristics study of the Aleppo pine needles powder before and after extraction of essential oils for further use in one of the aforementioned areas.

## MATERIALS AND METHODS

### Supply of plant material

In this work, the plant material needles of Aleppo pine tree (AP) (Fig. 3c) are collected in spring, from the park Tazekka, in Taza-Region Fez-Meknes (Morocco) (Fig. 2). This area is classified as a warm, summer Mediterranean climate according to the Koppen-Geiger climate

classification. The annual mean precipitation is 563 mm, and the mean annual temperature is 17.9 °C/64.3 °F (Mahmoud et al. 2021).

### Physical preparation of plant material

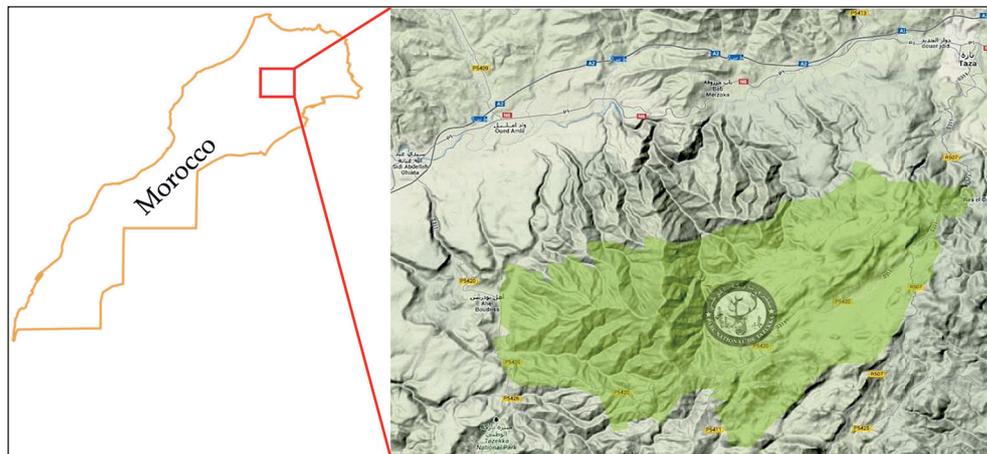
The Aleppo pine needles (Fig. 3b) were air-dried for one week and then dried in the oven at 37 °C, cut manually and then ground with a blender to a particle size of less than 1 mm. The powder obtained (Fig. 3a), sieved through a sieve with a mesh diameter equal to 1 mm, constitutes the biomaterial studied (AP)

### Biomaterial characterization method (AP)

#### Physicochemical analysis

The AP material was characterized by measuring physicochemical parameters (Ph, electrical conductivity EC, density, organic matter CO, total nitrogen Kjeldahl NTK, Phosphorus, some metallic elements; Fe, Mn, Mg,...).

The humidification rate was analyzed according to ISO 11465 (1993). The hydrogen potential was measured with a pH meter type HANNA.



**Figure 2.** Geographic location of Tazekka Park (Johnson et al. 2020; Hjouji et al. 2021)



**Figure 3.** Preparation of the biomaterial (Aleppo pine) (a) Aleppo pine tree, (b) needles, (c) sieved powder

The preparation of the solution for the measurement of the electrical conductivity was carried out according to the standard ISO10390 (2005). This measurement was done with a conductivity meter type HANNA EC 214. The density was evaluated using a pycnometer following ISO 18753-2017. The organic matter was analyzed by calcination using a muffle furnace type Barnstead Thermolyne 1400 °C, according to the Walkley method by applying the standard ISO 14235-1998. The mineral matter and the total organic carbon were deduced from the organic matter according to the NF EN 13039-2011 standard. The determination of the total Kjeldahl nitrogen (TKN) took place using a distiller type selecta nitro-pro, according to ISO 11261-1995. The metal elements were analyzed by the inductively coupled plasma technique (ICP-AES) after mineralization of the solid sample to put it in a solution.

#### *Spectroscopic analysis of the biomaterial (AP)*

We analyzed the biomaterial AP by X-ray spectroscopy (XRD), infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) associated with energy X-ray detection (EDS) type Quanta-200. We analyzed the powder of Aleppo pine needles by SEM before and after the essential oil extraction.

#### **Method of extraction of the essential oil from the biomaterial AP**

We performed the extraction of the essential oil by steam entrainment using hydro distillation. After placing 500 g of AP biomaterial in a flask with one liter of distilled water for 4 hours, we brought the system to boiling point by heating it until the distillate was completely clear. The resulting extract was passed through anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) to remove traces of water, and then we collected it in an amber-colored bottle away from light to avoid rapid oxidation and stored it in a refrigerator at 4 °C for later use (Hjouji et al. 2021).

We determined the essential oil chemical composition by gas chromatography coupled

with mass spectrometry (GC/MS), as we did in our previous work (Hjouji et al. 2021)

## **RESULTS AND DISCUSSION**

### **Identification of the AP biomaterial**

#### *Physicochemical characterization*

The biomaterial is less dense, acidic in character, weakly conductive, composed of a few metallic elements in the decreasing order  $\text{Na} < \text{Ca} < \text{Mg} < \text{K} < \text{Al} < \text{Zn} < \text{Fe}$  (Table 1). Its humidity of about 41.06% indicates that it is porous with considerable hygroscopic capacity.

#### *Spectroscopic characterization*

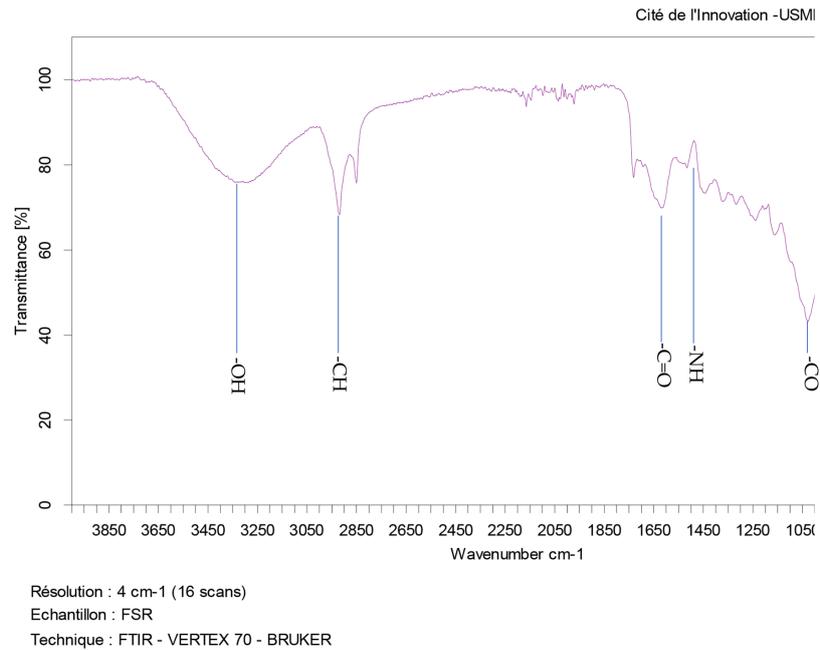
##### *Infrared spectrometry*

Infrared spectroscopy performed for the biomaterial AP (Fig. 4) showed the presence of peaks: The  $1040 \text{ cm}^{-1}$  peak attributed to alcoholic stretching vibrations ( $-\text{CO}$ ). The peak at  $1400 \text{ cm}^{-1}$  is attributed to bending ( $\text{NH}$ ). The strong peak at  $1650 \text{ cm}^{-1}$  can be attributed to the valence vibration of the ( $\text{C}=\text{O}$ ) carboxylic group, present in lignin and hemicellulose (Sain and Panthapullakkal 2006). A peak that extends between  $2700 \text{ cm}^{-1}$  and  $3050 \text{ cm}^{-1}$  and centered at  $2950 \text{ cm}^{-1}$  is related to the elongation vibration of the ( $\text{C-H}$ ) cellulose bond. A broad and strong band is found between  $3050 \text{ cm}^{-1}$  and  $3650 \text{ cm}^{-1}$  and centered at  $3300 \text{ cm}^{-1}$ , possibly due to the overlapping of the aromatic and aliphatic phenol structures ( $\text{O-H}$ ) stretching, lignin and cellulose group (Benyoucef and Harrache 2015).

This analysis also showed the presence of aromatic compounds and ketone fingerprints relating to the presence of cellulose, pectin, lignin, hemicellulose, and furfural (Benouadah et al. 2019). Thus, the surface oxygenated functional groups well explain the acidic character of the biomaterial.

**Table 1.** Physicochemical parameters of the biomaterial P.A (*Sinus Halepensis*)

Parameter	pH	H (%)	D	CE ( $\mu\text{S}/\text{cm}$ )	Fe (mg/L)	P (mg/L)	Mg (mg/L)
Value	4.32	41.06	0.6	1181	0.02	0.11	0.82
Parameter	Mn (mg/L)	Ca (mg/L)	Na (mg/L)	K (mg/L)	Zn (mg/L)	Cu (mg/L)	Al (mg/L)
Value	<0.01	2.41	2.43	0.58	0.07	<0.01	0.23

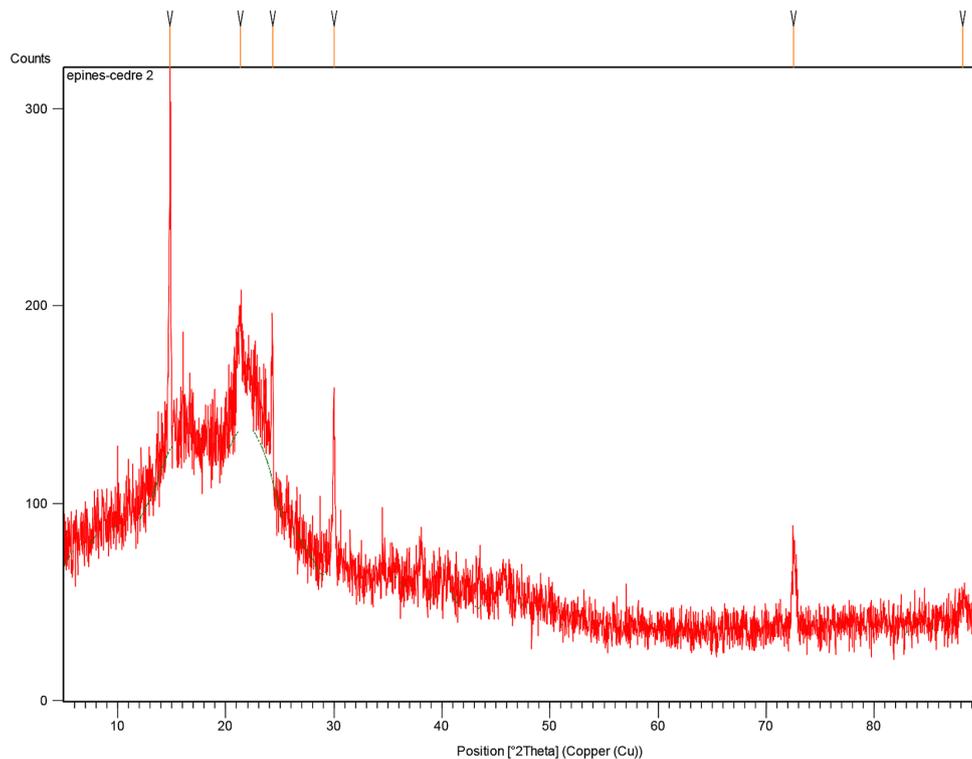


**Figure 4.** Infrared spectrum of the biomaterial AP

#### *X-ray diffraction (XRD)*

In order to identify the structure of our biomaterial whether it is crystalline or amorphous and to determine the crystalline phase(s) to which it belongs, we performed X-ray diffraction without any chemical treatment. The diffractogram of the AP biomaterial presented in (Fig. 5) shows a more

intense peak at  $2\theta = 21^\circ$ , which corresponds to polyethylene and cellulose, also the XRD diffractogram indicated the presence of two peaks at  $15^\circ$  and  $72^\circ$  attributed to polyethylene and cellulose, respectively, note that at about  $15^\circ$  we observed an amorphous halo, suggesting the semi-crystalline nature of the biomaterial (Haddadou et al. 2015).



**Figure 5.** Diffractogramme X of the biomaterial P. A

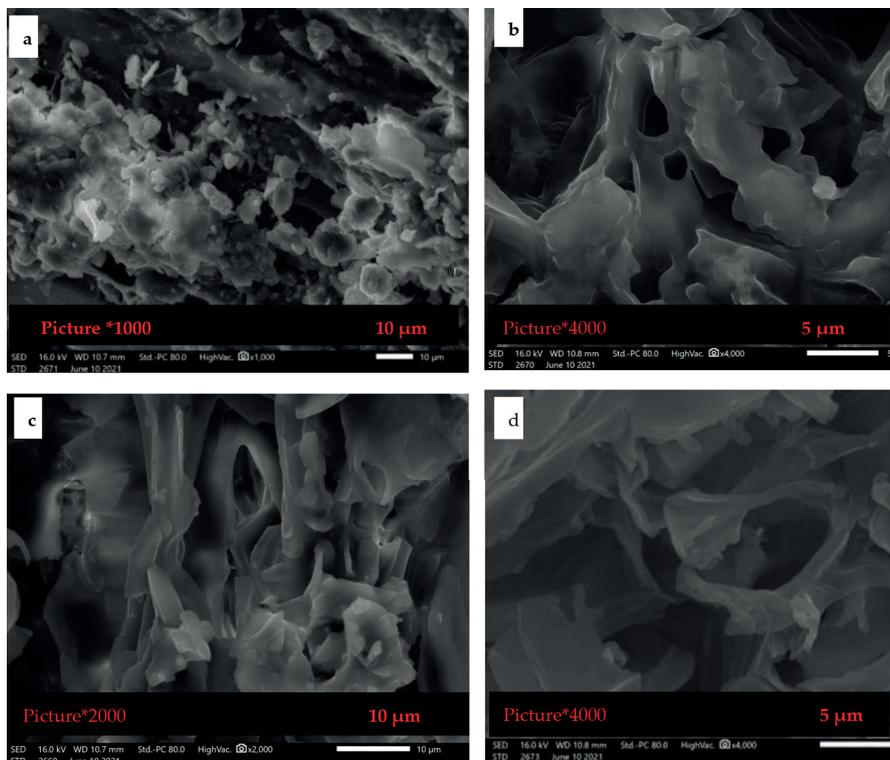
### Scanning electron microscopy (SEM)

The analysis of the AP biomaterial by scanning electron microscopy allowed us to observe its texture and characterize the mineralogical assemblies.

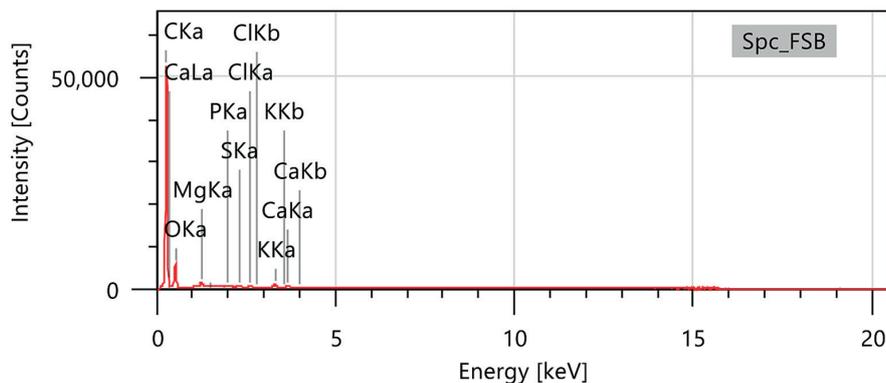
The micrographs obtained with different magnifications before and after the essential oil extraction (Fig. 6) show that the AP biomaterial is porous. This porosity has increased after the essential oil extraction, giving evidence of the specific surface increase of the studied biomaterial. These characteristics provide to our biomaterial as an adsorbent character to the air or water pollutants.

The semi-quantitative analysis by EDX of the biomaterial AP indicated its composition in

majority products; carbon (79.91) and oxygen (18.91), and other elements in weak proportions (Mg: 0.37), (Al 0.04), (P: 0.12), (S: 0.14), (Cl: 0.09), (K: 0.28), (Ca: 0.14) (Figure 7 and Table 2). The results thus obtained corroborate the results found by DRX and IR and show that the large part of the biomaterial is made up of organic molecules that could be extracted. It has been proven that the chemical composition of Aleppo pine needles can have a change if it's exposed to pollution such as the accumulation of certain heavy metals (Szwed, Żukowski, and Kozłowski 2021). Fortunately, in our study area we found the absence of any industrial activity that could affect the quality of our biomaterial.



**Figure 6.** Scanning electron microscope observation of the AP biomaterial (a, b before the essential oil extraction; c, d: after the essential oil extraction)



**Figure 7.** Energy dispersive spectrum (EDX) of AP biomaterial

**Table 2.** Elements constituting the biomaterial AP

Element	Line	Mass%	Atom%
C	K	73.82±0.06	79.91±0.06
O	K	23.26±0.10	18.91±0.08
Mg	K	0.70±0.01	0.37±0.01
Al	K	0.09±0.01	0.04±0.00
P	K	0.29±0.01	0.12±0.00
S	K	0.34±0.01	0.14±0.00
Cl	K	0.24±0.01	0.09±0.00
K	K	0.83±0.01	0.28±0.00
Ca	K	0.43±0.01	0.14±0.00
Total		100.00	100.00
Spc_FSB		Fitting ratio 0.0130	

### Identification of the essential oil of the biomaterial AP

The essential oil extracted from AP biomaterial by hydrodistillation is colorless, transparent with a strong odor. The extraction rate is important,

it is about 0.65 %. The analysis of this essential oil by chromatography (GPC/MS) showed the presence of 21 compounds, of which 8 are the main ones, in decreasing order: Caryophyllene (32.97%);  $\alpha$ -pinene (13.72%);  $\beta$ -pinene (11.02%); Alpha-humulene (7.86%); Cembrene (6.13%);

**Table 3.** Chemical composition of the essential oil of biomaterial AP

Pic	Compound	R. time	Area %	%
1	$\alpha$ -Pinene	7.805 7.957	13.72	12.5
2	1R- $\alpha$ -Pinene	8.035	5.00	3.68
3	Sabinene	8.990	1.15	1.21
4	4(10)-Thujene	9.146	1.09	1.17
5	$\beta$ -Pinene	9.417 9.473 9.609	11.02	13.74
6	trans- $\beta$ -Ocimene	11.033 11.130 11.303	5.31	6.65
7	4-Isopropylidene-1-cyclohexene	12.319 12.507	2.68	4.32
8	Copaene	20.788	0.88	1.69
9	Caryophyllene	22.044	32.97	15.87
10	$\alpha$ -Bisabolene	22.673	1.07	1.53
11	$\alpha$ -Humulene	22.879	7.86	9.19
12	isovalerate de $\beta$ -phenylethyl	23.359 23.485 23.627	4.43	7.89
13	$\alpha$ -Murolene	23.889	0.83	1.39
14	$\alpha$ -Cadinene	24.375	1.01	1.83
15	$\alpha$ -Bisabolene	24.908	0.74	1.28
16	Caryophyllene oxide	26.208	0.82	0.85
17	Guaiol	26.599	0.55	0.89
18	Caryophyllene-(11)	28.288	0.38	0.61
19	Cembrene	34.841 35.146	6.13	9.84
20	Cembrene A	35.485	0.72	1.22
21	Thunbergol	37.296	1.62	2.69

trans-beta-ocimene (5.31%); 1R – alpha-pinene (5.00%) and beta isovalerate – Phenylethyl ester (4.43%) with a total percentage of 83.78 %. The rest of the compounds were at lower levels (Table 3). Thus by comparing this chemical composition with that found by other researchers in other plants we can say that these essential oils may have several properties such as antibiofilm, cytotoxic, and anti-acetylcholinesterase activities (Caputo et al. 2022). Moreover the high content of Caryophyllene has given some essential oils antifungal and antimycotoxic properties (Scanavacca et al. 2022).

## CONCLUSION

The biomaterial characterized in this study was prepared from the powder of Aleppo pine (*Pinus Halepensis*) needles. The physicochemical, spectroscopic, and microscopic analyses of this biomaterial have shown that the biomaterial AP is less dense, poor conductor, porous, acidic, weakly composed of mineral elements and mainly composed of carbon and oxygen. Thus, groups of carbonyl compounds (ketone, aldehydes) and aromatic compounds could be formed and confer to the AP biomaterial the characteristics of absorbent. The exploitation of these needles will surely avoid their accumulation in the forests and thus reduce the risk of wildfire outbreak.

The essential oil extracted from this biomaterial is rich in caryophyllene,  $\alpha$  and  $\beta$  Pinene, Cembrene, and  $\alpha$ -Humulene which could be used in food, pharmaceutical and cosmetic fields.

This study is useful to foresee the fields of application of the AP biomaterial in its raw state or after extraction of the essential oil such as the treatment of wastewater, air, either as an absorbent or filter, the elaboration of organic amendments, or it can be used as a component of insulating materials or cellulosic concretes.

As perspective, we shall study the kinetics of adsorption of this biomaterial after calculating its specific surface and determine its regeneration capacity.

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