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Characterization and valorisation of olive by-products from a traditional oil mill in Béjaia.

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ABSTRACT/RESUME

Abstract: *In Algeria, the olive oil extraction generates enormous quantities of olive-growing by-products: the olive residue and margines. So, the characterization and the valorization of these by-products seem of great importance. The first shutter consists in characterizing the whole of fractions resulting from the centrifugation of the margines (liquid rejection) to knowing the liquid phase, the oily phase and the solid phase as well as the olive residue, with various physicochemical techniques of analysis available on the scale laboratory. The liquid fraction which was characterized shows a very strong organic and mineral matter concentration being able to be used in irrigation either directly, or diluted with water after having undergone physicochemical and biological treatments, enriching the composition and texture by the arable lands (fertilizing contribution). As for the oily fraction the results show a very good nutritional quality from the point of view analyzes physico chemical, dedicated to being used like salad oil or in our work, it was used for obtaining a dry soap.*

I. Introduction

In addition to oil as the main product, the olive industry produces large quantities of by-products; liquids called vegetation water or margines; and solids called pomace. Thus, 100 kg of olives produce an average of 35 kg of pomace and 100 litres of margines. In addition, the size of the olive tree gives an average of 25 kg of leaves and twigs annually [1].
The liquid wastes (margines), raise a serious environmental problem. They are overloaded with organic matter, minerals and poly-phenols. They are often discharged into sewers, stored in evaporation basins or spread directly on the ground without any prior processing. This has a negative impact on the environment in the form of clogged soils, pollution of surface and ground water by infiltration and the release of noxious odours. In addition, the presence of polyphenols, responsible for phytotoxic and antimicrobial effects, makes biological treatment ineffective.
However, solid wastes (pomace) present less danger than margines. They still contain a certain percentage of fats that varies according to the type of olives and the conditions of oil extraction. The extraction of pomace oils makes it possible to give a certain added value to the production of olive oil.
To eliminate or diminish the pollution caused by the margines, several physical, physico-chemical, advanced oxydation, biological and valorization treatment techniques have been developed and used. Some of these techniques do not remove all the pollution; others are often costly or generate secondary pollution that requires another subsequent treatment.
The recycling of these residues became an ecological and economical requirement. Indeed, it will allow the reduction of increasingly significant pollution and contribute to improving the profitability of the sector, especially in the southern Mediterranean countries.

II. Materials and methods

Margins have a highly polluted waste in the form of a residual liquid of variable composition depending on the type of olives, their degree of ripeness, the farming and exploitation process, the salting practice to preserve the olives, the climate conditions and the olive oil extraction process [2]. Margins are also

characterised by a foul-smelling odour which becomes more intense as they are stored.
In this study, we have chosen a traditional process of extracting Chemlal type olive oils which, occupies almost all of the orchards (90%) harvested in the SEDOUK region of Béjaia, this variety is considered as an essential variety, by its adaptation to the natural conditions of this region.
The samples of the water collected are intended to be characterized and valued inorder to obtain a hard soap, going through several stages
.
To obtain different fractions of margine discharges from the traditional process (from BEDJAI), we carried out a centrifugation for 20 minutes at a speed of 4500 rpm, which allowed us to obtain the following fractions:

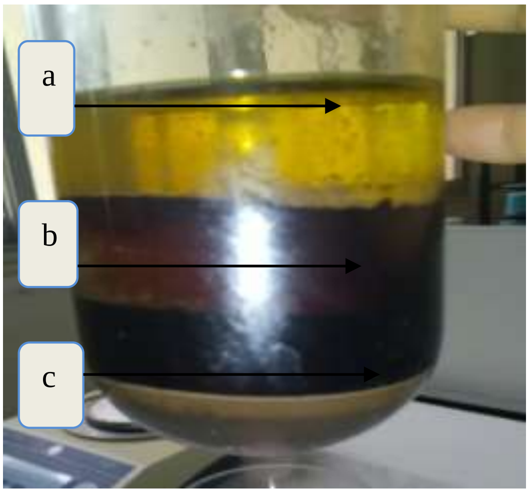

Figure N°1. *Fractions obtained after centrifugation of the margines*

a/ Oily fraction 18,90%
b/ Liquid fration 59,18%.
c/ Solid fraction at 20.83% , with a loss equal to 1.09%

These rates mean that the margine is very rich with organic and mineral matter, which is highly dependent on the mode of trituration.
Margine is subject to a successive series of physico-chemical analysis such as: pH, suspended matters (SM), dry mineral matters (DMS) and volatile matters (VM), biological oxygen demand (BOD_5), chemical oxygen demand (COD), phenolic compounds, conductivity, salinity, calcium, magnesium, chloride and heavy metals, while the obtained oily fraction is subject to several physico-chemical analysis such as : the saponification index, acidity index, ester index, the acidity, the pyroxide index and for a possible valorisation, the oily fraction is dedicated to the production of a hard soap which undergoes a wide range of analysis such as: pH, water content, active ingredient rate and foaming power.

III. Results and discussion

III.1. Liquid fraction characterization

The obtained results are shown in the table below.

Table N°1. *Liquid fraction physico-chemical caracteristics*

Parameters	Results
pH	4,79
MS (g. l^{-1})	85,434
DMS (g. l^{-1})	9,11
VM (g. l^{-1})	76,324
COD (mg d'O_2.l^{-1})	9099
BOD_5 (mg. l^{-1})	67,2
Phynolic compounds (µg EAG/l)	36,45

The dry mineral matter content of margines is of the range of 9,11 g. l^{-1}
The Volatile Matter represents 90% of the DM (dry matter) which is 76,324g. l^{-1}. This shows the presence of certain volatile organic compounds in the margines. This proportion is close to that observed by many authors (24g/l ±2; for the Dry Mineral Matter and 114g/l ±2 for the Volatile Matter) [3,4].
The average organic matter content expressed as COD is about 9,099 g of O_2.l^{-1}. This shows the strong oxygen requirement for the complete oxidation of organic matter contained in this effluent and the presence of organic compounds that are hardly biodegradable.
However, our value is still comparable to those obtained by several authors in the margines issued from the centrifuge system [5-8].
With a high charge of organic matter as all liquid waste from food processing activities. This load is given by a BOD_5 of 67.2 mg of O_2 /L after filtration, which characterizes the total oxidizable pollution.
According to Ouzounidou et al [9], the BOD_5 in oxygen has a value of 110 g O_2/l.
These releases are also marked by the predominance of toxic substances, particularly phenolic compounds, which are of the order of 36.45 µg EAG/l, which gives them a valuable antimicrobial power (9.7 g. l-1) according to Renalli et al [10].
This high level of concentration could limit any natural biodegradation, and therefore could lead to a more or less significant disturbance of the entire ecosystem. Nevertheless, it is close to that mentioned by Kissi and al [11].

Table N° 2. *Mineral composition of the liquid fraction*

Parameters	Results
Conductivity (mS.cm^{-1})	13,73
Salinity (g/l)	9,611
Calcium (g. l^{-1})	1,75
Magnesium (g. l^{-1})	0,95
Chloride (g. l^{-1})	24,85

The mineral composition of these margines has shown that these wastewaters have a high charge of ions, particularly due to the presence of ions such as cations and anions, like sodium chlorides, probably related to the salting practised in some of them or because of the natural high content of mineral salts in the olives [12].
These results are too high and exceed the permissible discharge limit (7.00 ms/cm), but they are adequate in comparison to the range reported by Benrouina and al [13]. Such a value reflects the high content of salts present in these liquid wastes.
The margines are rich in Ca^{+2}, Mg^{+2}, These results are similar to those mentioned in literature [14]. Ca^{+2} content is close to that found by Aissam et al [15] which is in the order of 2 g.l^{-1} for Ca^{+2} and 1.3 g.l^{-1} for Mg^{+2} ; that are higher than those recorded by Mounia Achak and al [16]. However, the concentration obtained in our study remains lower than that observed in the margines of small oil mills where the preservation of olives in salt is imposed by lack of plant capacity.
This richness in mineral elements has led many researchers to orient the treatment of the margines towards their valorization in compost or by fertilizing agricultural land [17-18].
The obtained results are close to those found by Ouabou and al [19]. This high concentration is due to the addition of salt in large quantities for the preservation of olives or the richness of the water used during trituration.
Table N° 3. *Liquid fraction metal composition*

Parameters	Results
Cd	<1µg/l
Cr	211.6µg/l
Cu	746.5µg/l
Fe	11960µg/l
Mn	2828µg/l
Ni	<1µg/l
Pb	72.89µg/l
Zn	5361µg/l

By analysing these results we can remark clearly that the margines contain non-negligible levels of metals, in particular: Fe (11960 µg/l) and Zn with (5361µg/l).
In fact, these metals are vital trace elements that are part of the mineralogical constitution of olives. However, Cr and Cd have an exogenous origin. So, the metal composition of the margines depends on the quality of the olives triturated especially for Zn, Cu and Fe.
The results of this metallic characterization are compatible with those obtained by Zenjari and al [20]. Heavy metals such as copper (Cu), cadmium (Cd), chromium (Cr), plumb (Pb) and nickel (Ni) are found in trace quantities.

III.2. Oil characterization
The obtained results are reported in the table below.
Table N° 4. *Physico-chemical characteristics of the analysed oil.*

Parameters		*Results*
IS (mg/g)		203.316
Normes	C.A C.O. I	184- 196 184- 196
I.A (mg/g)		1.262
Normes	CODEX STAN 210-1999	0.6- 4 mg de KOH/g
IE (mg/g)		202.099
A %		0.631
Normes	C.A C.O. I	3.3% 3.3%
IP méq. O_2/Kg		7.33
Normes	C.A C.O. I	20meq ofO_2/Kg of oil 20meq ofO_2/Kg of oil

The saponification index is in the order of 203.361 mg KOH/g of oil. This value exceeds the threshold value authorised by the standards established by the International Olive Council (C.O.I) and the Codex Alimetarius (C.A), which explains the high richness of our oil in short chain fatty acids.
The analysis of the results of table N°4 indicates that the acidity of the oil tested is consistent with the CODEX STAN 210-1999 standards (0.6 - 4 mg KOH/g), so this oil can be used for consumption, and for the production of soaps.

The acid index given by the free acidity enables to control the level of hydrolytic, enzymatic or chemical degradation of fatty acid chains.
This index is also related to the olive sanitary quality, mastering of the technological process implemented for the conservation, storage and processing of the primary material, and to the degree of maturity of the fruit [21].
The variation in the obtained results can be explained by the maturity of the fruits and the origins of the olive trees [22].
And since the ester index is the difference between two indices (the saponification index and the acid index) which, in our case, are within the standards.
According to the norms of the International Olive Council, 2015 about the free acidity, we can observe that the value of this latter remains within the established limits, which is between 1 and 3.3% and enabling it to be classified in the category of virgin olive oil.

The results reported in the table indicate that the peroxide index (PI) of this oil is 7.33 meq O_2/kg, which meets the standards set by COI (2015) recommending a peroxide index less than or equal to 20 meq O_2/kg.
Some lipid degradation processes are obviously due to the different processes applied to the olives from the field to the oil mill during the stages that precede oil extraction (harvesting, storage of the olives, extraction), which could be the cause of the increase in acid and peroxide indices.
The oil obtained by centrifugation and thus characterized; for a possible valorization, it is intended for the preparation of hard and liquid soap, by adding to it the convetable base NaOH and KOH respectively.

III.3. Soap characterization

Table N° 5. *Analysis results carried out for soaps*

Soap	Hard soap	Liquid soap
Humidity Rate (%)	18, 34	26,53
pH	9,56	11,9
T°C	22,6	22,3
Active matter content %	62.38	/
The free alkali content (%)	20	30
Monsoon power (max. value) ml	420	310

The recorded humidity levels for both types of soap: liquid and hard, are in accordance with the ISO 672 -1978 standard, which sets a tolerance threshold of between 14 and 20% for toilet soap and 55% for soap paste.
The contents of free alkalis obtained are respectively: 20% for hard soap, which meets the ISO 456-1973 standard (20%) and 30% for liquid soap, which is much higher.
The pH of prepared soaps varies between 9.5 for hard soap and 11.9 for liquid soap, which shows their basic characteristics.
The richness of those latter in fat with 8% of surgras, allows more recovery of the protective film of the skin and its protection against irritations. According to these results, we observe that the pH of the hard soap meets the standards of liquid detergents and powder detergent (ISO 8212-1986 standards whose pH value varies between 7 to 11), while the liquid soap is slightly higher than this standard.

The active matter content of the hard soap is 62.38%, which means the richness of this latter in fatty acids of great detergent power, especially on the dirt and the protective effect of the user's skin.
The obtained results about the foam show that the produced soaps have a good monsoon power, mainly due to the nature of fatty acids existing in olive oil, which gives the soap a good monsoon power in cold state and in the absence of additives such as: EDTA that makes commercial soap soft.
The washing test shows that our hard soap washes spots well (standard: blood, coffee, tomato and mix...), and gives practically similar results to those obtained by the Marseille soap produced by the detergent universe (Aigle).

III.4. Characterization of olive pomace powder (flour)

The olive pomace thus recovered by this oil mill is crushed into fine particles called flour, whose characteristic parameters are: pH, moisture content, dry matter, organic matter, ash content and fibre content.

Table N° 6 . *Parameters characterizing olive pomace flour.*

Parameters	Results	standards
pH (avg)	4,74	5,15 [23]
H.C% (avg)	6,99	/
D.M % (avg)	93,01	60-76 [24].
O.M % (avg)	95,41	/
A.C% (avg)	4,59	4-6 [24].
T.F% (avg)	9,5	/

avg: average, H.C: Humidity Content;
D.M.: Dry Matter; O.M.: Organic Matter;
A.C.: Ash Content; F.C.: Fiber Content.

According to the obtained results, we note that the pH variation of the dried and crushed pomace from this oil mill (BEJAIA) is too acidic, which explains the richness of these pomace in fatty acids.
The dry matter content is high, it is around 93.01%. This content increases gradually during the storage period. From one hand It can be justified by the production of proteins and ffrom the other hand by the multiplication of yeasts and moulds [25] and the evaporation of a considerable quantity of water (humidity) and this according to the storage conditions (temperature, humidity of the environment, quantity of oxygen...).
Olive pomace, composed mainly of skin, stones and shell, is both rich in organic matter, mineral matter at different proportions, according to our results this can be justified by high contents of organic matter exceeding 90%, ash contents exceeding 4% with average fiber contents of 9 to 10% in its various fractions [24].

This pomace is intended for the use as natural adsorbents in future work, and the obtained flour can be used as an additive to bread flours (nutritional improvement and texture).

VI. General conclusion

Protecting the environment and controlling energy is one of the key elements of sustainable development, which is a major challenge for the future of mankind and the planet. Facing this, environmental degradation and climate change will affect humanity.

The Algerian will to commit itself in favour of renewable energy seems clearly considered, in particular by the research work started recently by our researchers in the field of valorisation of by-products.

The main forms of renewable energy are solar, wind and biomass energy. Among the most relevant substitution opportunities in Algeria, the biomass generated annually by the Algerian olive grove which is mentioned as a renewable energy source available for the eventual production of thermal, electrical and biogas energy following anaerobic fermentation of its waste, which can represent both environmental and economic benefits.

It is within this framework that this work has focused on the valorisation of the by-products of the olive industry, in particular.

Although there are multiple uses for raw olive pomace, given its chemical composition, which is still rich in edible oil, cellulose and nitrogenous materials, this waste raises serious problems for the environment. Their harmful effects derive largely from their content of polyphenols that are difficult to biodegrade.

Besides the olive pomace (solid part), the margines, the liquid waste from olive oil production, are discharged into rivers or sewers. Consequently, these effluents raise serious problems for the aquatic ecosystem because of their content of soluble phenolic compounds in its aqueous phase.

These aromatic compounds clog the soil, asphyxiate and inhibit the growth of living organisms.

Some authors have confirmed that margines can be used as a good fuel. Also, olive pomace is considered a renewable energy resource and also a good metal adsorbent due to its lignocellulosic composition.

A new alternative way is to use these margines mixed with a solid matrix to form a biomass fuel. Mixtures of olive pomace/margines and sawdust/margines have been prepared. The use of these mixtures as a fuel, as an organic amendment and in soap factories may present an alternative for the valorization of this type of waste, in relation to our results of characterization and valorization.

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