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ENVIRONMENTAL IMPACT FROM OLIVE MILLS WASTE DISPOSAL, CHEMICAL ANALYSIS OF SOLID WASTES AND WASTEWATERS

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Abstract

Producing of the olive oil is accompanied by relevant amounts of wastes: olive husk (OH) and olive mill wastewaters (OMW). Their disposal is a critical problem in the Mediterranean countries by reaching in one season approximately 10 - 12 million m^3. It has been shown that the disposal of OMW into surface waters brings to reduction of their biodiversity and their contamination due to high organic load and toxic substances such as polyphenols. This situation is evident in the regions where the olive oil industry operates. The national plan on olive planting, by tripling the area of olive plantations, hence the amounts of olive mill wastes is expected to be multiplied. During the harvesting season 2012 - 2013, the OMW amounts produced in Albania are considered to have reached in 50 - 52 thousand m^3, while the OH have reached approximately to 30 thousand tons.

The study was conducted in a three phase extraction olive mill, in one of the most intensive regions of olive cultivation, Mallakastra. It included in-situ analyzing of physico-chemical parameters of OMW and analysis of the trace metals in solid wastes was performed in the Laboratory by Atomic Absorption Spectroscopy (AAS).

The results show high content of potassium (K) 18.6 g/kg dried weight, and calcium (Ca) 3.70 g/kg and magnesium 1.9 g/kg, while presence of sodium (Na) was in minimal 600 mg/kg, the iron (Fe) reached values 512 mg/kg. The pH values of the OMW varied from 5.10 - 5.77, the Electrical Conductivity - EC values varied 6.46 - 8.82 mS/cm, while the dissolved oxygen (O_2) 1.40 - 2.30 mg/L.

Their disposal in none proper sites will have negative impact on the quality of the soil where they are disposed. It is imperative the implementation of legislation to the olive oil extraction industry by-products.

***Key words**: Olive oil, extraction industry, Olive mill wastes, Trace metals.*

1. Introduction

The world olive oil (OO) production is mainly concentrated in the Mediterranean countries, where the biggest olive producers are Spain, Italy, Greece, Turkey and Tunisia. Albania, as a Mediterranean country, is a producer of the olive oil. Recently, according the data on country' olive oil quantity has ranked Albania as 16th in world production (FAOSTAT [1]).

Production of the olive oil is very important for Southern European countries. It is, mainly, a product with closed production cycle, with direct important impact for remote and rural areas that show difficulties on the economy. Beyond the economic value, the olive oil production is accompanied by environmental problems. The extraction process produces large amounts of solid wastes, composition of olive husk and crude olive cake (OH) and olive mill wastewaters (OMWW), a mixture of vegetable and added technological water. The OMWW is a smelling acidic red-to-black colored, liquid of high conductivity. Its composition varies qualitatively and quantitatively according to the olive variety, climate condition, cultivation practices, the olive storage time and olive extraction process. It is composed of 83 - 92% water, 4 - 16 organic matter, and 1 - 2% minerals (Ben Sassi *et al*. [2]; Dermeche *et al*. [3]).

The disposal of OMWW is becoming a critical problem in the Mediterranean Sea Basin. The overall OMWW amount produced during a short period of time, from November to March, reach 10 - 12 × 10^6 m^3/year. Spain produces 20% of the total OMWW of the Mediterranean basin with 2 - 3 × 10^6 m^3 /year (De Ursinos [4]), while Italy contributes approximately with 3 × 10^6 m^3 /year (Vitolo *et al*. [5]).

Study was conducted in the Region of Mallakastra during the harvesting period 2012-2013. This region cultivates the autochthon cultivar, Kalinjoti, which is the main cultivar in Albania with more than 50% of total olive trees.

1.1 Olive oil mill waste regulation in Mediterranean countries

A number of EU laws regulate what should be done with wastes production by olive oil extraction industry. The Waste Framework Directive (2008/98/EC) includes rules on hazardous waste and waste oils and requires Member states to recycle at least half of their household and general waste by 2020. Liquid wastes from olive oil production fall under Urban Waste Water Treatment Directive 91/271/EEC, amended by Directive 15/98. The Directive 91/271/EEC incorporates collection, treatment and discharge of urban wastewaters. The directive deals also treatment and discharge of wastewater from certain industrial sectors, including olive oil production (Komnitsas and Zaharaki, [6]).

Also main EU production countries have implemented their national regulation on the olive oil extraction industry. Spain government has banned the discharge of OMWW into receiving waters. It has implemented two phase extraction technology, by reducing the OMWW. The Italian law allows spreading of OMWW on agricultural soils. In Greece there is no specific regulation regarding to the discharge of OMWW. It gave additional power to the Prefectures, implementing its policy (Erses Yay *et al*. [7]).

1.2 Extraction Industry in Albania

The olive oil industry in country has changed its organization after 1990. Actually it is organized in small private enterprises that are located in the regions of olive cultivation. During last decade in that sector are invested 11 million $ mainly in establishing of new factories with advanced technologies (MAFCP [8]). The overall installed capacity is approximately 88 tons/hour work. From the actual OO production it is estimated that only 1/3 of its capacity is exploited. The highest efficiency in olive oil production is reached mainly in Southern part of the country that includes: Saranda, Vlora, Mallakastra regions, and Central part that includes: Fieri, Berati, Elbasan and Tirana regions. In total they comprise more than 80% of the olive trees actually in production (MAFCP [8]).

Studies result of actually used olive extraction technologies, is that in Albania dominates the 3-phase technology and in limited numbers 2-phase extraction olive technology, and much less Pressing technology systems.

Beyond the concern on their negative environmental impact, these wastes contain valuable resources of organic matter and nutrients (Albuquerque *et al*. [9]).

2. Materials and Methods

2.1. Materials - Sampling of the OMWW and OH

The wet samples were taken from a three phase olive mill immediately after the extraction of the olive fruits and directly transported to the laboratory. Each of them was divided in two sub-samples. The OMH were dried to oven at 105 ^{0}C for 24 h to determine the moisture content, while the physic-chemical parameters of OMWW were analyzed upon their arrival to laboratory.

2.2 Methods - Analytical methods

In the OMWW were determined the electrical conductivity (EC), dissolved oxygen and pH. The dried sample was taken in raw material and washed polyethylene bag to prevent the contamination. It was dried up in oven at 105 ^{0}C and milled. The sample was prepared for further analysis in cold extraction. It was weighed 1g dried sample in Erlenmeyer (100 mL) and consequently was added 20 mL mixture HCl (cc) and HNO_3 (cc) (1 : 1). The mixture was kept through the entire the night, and after 24 hours is filtered. After that the sample was passed in a standard 50 mL balloon, and after was passed in Teflon bottle. The metals in the sample were analyzed in different wavelengths with the technique of spectrophotometer with atomic absorption. Metals: K, Na, Ca, Mg, Fe, Cu, Mn and Zn were analyzed by atomic absorption spectrophotometry (AAS).

3. Results and Discussion

According to equation proposed by De Ursinos *et al*. [4], the amount of olive wastes produced in Albania during the harvesting year 2012 is approx. 60 × 10^6 kg OH and 125 - 137 × 10^6 kg OMWW. Actually, in Albania do not exist any extraction plant to use olive cake as raw material to extract the remaining olive oil. From our analysis results that the reaming percentages of the olive oil in the olive paste reach up to 8%. In addition there is a lack of awareness from the producers and Legal institution regarding to the environmental pollution from the olive oil extraction industry. Vegetable waters are discharged directly to the surface streams, while olive husk is used as food staff to animals or in some case is dried up and used as calorific source in different situations.

The extraction procedure employs discontinuous (pressing) or continuous (centrifuging) technologies.

The discontinuous process is the oldest technology employed from the olive mills. This method offers advantage regarding to small water quantities produced, which ranges from 40 - 60 L/100 kg olive fruit. The OMWW produced by this process show higher chemical oxygen demand compared to the OMWW generated by other processes (Dermeche *et al*. [3]). The continuous olive oil extraction process uses industrial decanter to separate all the phases by centrifugation. It can operate as two-phase or three-phase systems. The continuous three-phase decanter produces a larger quantity of OMWW, 80 - 120 L/100kg olive fruits. This system is advantageous due to complete automation, and smaller area equipment, but disadvantageous regarding to the higher amounts of water and energy consumption, and large amounts of OMWW outputs. The two-phase extraction process has been introduced in 1990. It aims to minimize the volume of the OMWW. The olive paste is separated into two phases: olive oil and wet pomace. The wet pomace is semi-solid by-product. It is difficult to manage because of its pollutant load are very concentrated. This technology is dominant in Spain (Beaufoy [10]).

The risk of pollution by olive mills appeared especially in the case of 3-phase centrifugation procedures. The amount of vegetation water produced upon the milling processes vary from 40% OH - 40% OMWW in the traditional batch mills, to 50% OH - 95 OMWW% in the continuous-centrifugation systems [11].

The olive mills in Albania, actually in operation are 131. They are scattered in different regions close to the areas of olive plantations. Related to the applied extraction techniques in the olive mills are used two phase separators (MAFCP, [8]).

Table 1. Key figures on Oil and by-products related to the extraction technology

Production process	Input	Amount of input	Output	Amount of output
Pressing system	Olives	1 t	Oil	200kg
	Washing water	0.1 - 0.12 m^3	OH*, OMWW**	400 kg 400 - 600 l
Three-phase decanter	Olives	1 t	Oil	200kg
	Washing water	0.1 - 0.12 m^3	OH,	400 kg
	Fresh water for decanter	0.5 - 1.0 m^3	OMWW	1000 - 1200 l
Two-phase decanter	Olives	1 t	Oil	200kg
	Washing water	0.1 - 0.12 m^3	OH, OMWW	500 - 600 kg 85 - 110 l

*OH - Olive husk; **OMWW - Olive mill waste waters (Caputo *et al.* [12]).

According to the strategic plan, in 2016, the olive production will reach to 135100 tons. This is equivalent with a triple amount of the data presented actually by olive mills.

A characteristic of the olive oil industry is its distribution in small size mills. A similar situation is present in Albania. Due to these characteristics it is difficult to apply environmentally friendly schemes for the waste disposal. Actually in Albania the OHs are burned close to the olive mills, while the OMWW are discharged in surface waters: rivers and ponds.

Due to high organic load and the presence of toxic substances such as polyphenols, the contamination of groundwater and surface waters is evident in the regions where the olive oil industry operates.

Main characteristic of the OMWW is: high organic load, high inert COD, low pH, and plant toxicity. The complex organic substances are generally resistant to biodegradation posing negative environmental effects and posing threat to aquatic life. Polyphenols present in OMWW may affect the enzymatic activity and fish reproduction via inhibition of neurotransmitter receptors and enzyme. No EU legislation exists in EU level to assess phytotoxicity of phenols (Justino *et al*. [13]).

As result, the disposal of the OMWW into rivers leads to the reduction of their biodiversity. The solid constituents of the wastes and the oil found in them cover the riverbed, by becoming it inactive. A lot of hydroid organisms absorb the solid constituents of the wastes. As results most sensitive organisms immediately move away or die from suffocation (Niaounakis and Halvadakis [14], Schmidt [15]). OMWW present a high biological and chemical pollutant load (BOD in the range 23 - 100 g/L). The BOD is 25 - 80 times greater than pollution level of common municipal wastewater (Anastasiou *et al*. [16]).

The results of physical-chemical parameters are presented in the Tables 2 and 3. They show that the pH values vary in acidic range, with mean value 5.45. The value of the Electric conductivity (EC) resulted in a mean value 7.71 mS/cm, while the dissolved O_2 resulted in mean value of 1.85 mg/L. Different authors suggest the discharge of vegetation waters in arable lands in maximum quantities of 800 m^3/ha (De Ursinos [4]). Meanwhile it is possible to apply the septic pond construction where vegetation water has to be collected and kept to evaporate (Komnitsas and Zaharaki [6]; Anastasiou *et al*. [16]).

Table 2. Physical-chemical parameters of OMWW

Parameters	Mean	Range
pH	5.45	5.10 - 77
EC (mS cm^{-1})	7.71	6.46 - 8.82
Dissolved O_2 (mg/l)	1.85	1.40 - 2.30

Table 3. Physical-chemical parameters of OH

Parameters	Mean	Range
Moisture (%)	51.43	50.62 - 53.52
Ash (%)	1.77	1.72 - 1.83

The analysis of metals in solid residues of olive oil extraction shows that the main element was potassium (K) with values of 254.85 mg/kg, followed by sodium (Na) 142.2 mg/kg, Mg 20 mg/kg, and Ca 17.05 mg/kg dry weigh of solid wastes (Table 4).

Table 4. Main characteristics of the OMWW and OH (mg/kg)

Parameters	Mean	Range
Na (mg/kg)	142.2	137.3 - 147.5
K (mg/kg)	254.85	234.51 - 275.43
Zn (mg/kg)	1.15	1.02 - 1.34
Fe (mg/kg)	12.85	11.35 - 14.45
Cu (mg/kg)	6.80	5.70 - 7.68
Mn (mg/kg)	1.50	1.25 - 1.89
Mg (mg/kg)	20.00	19.20 - 21.05
Ca (mg/kg)	17.05	16.35 - 17.82
Cd (mg/kg)	<0.5	< 0.5
Pb (mg/kg)	6.40	6.14 - 6.78

Comparison of the data from the OH with different origins indicates that the metal presence show similar values with results from different publications (Albuquerque *et al*. [9]; Abu Khayer *et al*. [17]).

4. Conclusions

- The amount of waste disposal produced by olive oil extraction industry is calculated to have reached approx. 60 × 10^6 kg OH and 125 - 137 × 10^6 kg OMWW for the harvesting year 2012 - 2013. These by-products actually are not used as raw material to extract the remaining olive oil. We have concluded on the actual situation that there is a lack of involvement to governmental bodies to deal with the environmental pollution from the olive oil extraction industry. The vegetable waters are discharged directly to the surface streams. The olive husk is used as food staff to animals and burned as calorific source.

- It is important applying of the technological schemes according to the Environmental legislation related to food industry wastes and especially to the olive mill wastewaters. The negative impact is present in the regions were the olive oil extraction Industry operates. The results show that the OM effluents presented high acidic values and rich in K, Na, Ca and Mg. Actually the husk are burned which mean permanent local air pollution. But it has to come in evidence the odor problem in that case. A proposal to the husk removal may have been their use as energetic source, and for animal feed.

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