A new olive oil production scheme with almost zero wastes

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ABSTRACT

The treatment and disposal of olive mill waste are among the most important environmental problems in the Mediterranean region, where the olive tree is mainly cultivated. Olive oil mill wastes are characterized by a high organic and inorganic load, expressed in COD and BOD values. In addition, the presence of organic components, such as phenols, low nitrogen concentration and high concentrations of slowly biodegradable compounds such as tannins and lipids make the processing of liquid wastes of oil mills very difficult. In Greece, annual olive oil production has quadrupled over the last 40 years because of the significant income that farmers have from the marketing of extra virgin olive oil. However, together with the production of olive oil the amounts of liquid and solids wastes were quadrupled as well.

The main objective of the present study is to develop a new scheme for olive oil production process with almost zero wastes, utilizing all the ingredients of the olive fruits to produce useful products and by-products, such as extra virgin olive oil, olive pomace oil, various antioxidants, animal feed, solid fuels and water for irrigation. The proposed new process involves separating the pulp by subtracting the whole olive kernel into a special separator. The kernel will be utilized for extraction of olive-residue oil with hexane and the remaining solid will be used as biofuels (pellet). From the paste, the phenols are first extracted, and the remaining paste is driven to a pilot oil extraction system consisting of a softener and two-phase centrifugation system (small olive mill extraction unit) to extract extra virgin olive oil and a semi-solid by-product (remaining part of the pulp, like the pomace). The latter residue will be subjected to an extraction process to obtain again a solution of phenolics but also of other organic substances as well as a solid edible phase. The solid edible phase after UV sterilization and other treatment will be partly used to produce an olive paste and the remains of animal feed. The solution of phenolic and other organic substances will be suitably processed into a membrane system to isolate and enrich phenolic substances that have nutritional and antioxidant value. The commercialization of phenols and other isolated byproducts can make a significant contribution to reducing the cost of the proposed process.

Key words: Olive mill extraction, olive mill wastes, membrane filtration, phenol isolation

INTRODUCTION

The olive tree is one of the ancient trees that gave food to the human. The history of the olive tree is strongly related with the Mediterranean countries and their culture [1]. The fruit of the olive tree is spheroidal or ellipsoidal (Figure 1) and can be divided to the wrist band and to the endocarp which is the kernel of the fruit. The wrist band is composed by the outer skin or Epicarb (a cuticular lipid layer) which reaches up to the 1.0 -3.0% of the fruit's weight and the mesocarp (flesh or pulp) which contains tissues rich in oil and water and reaches up to the 70-80% of the fruit's weight. The endocarp (or kernel or stone) reaches up to the 18-22% of the fruit's weight and is composed by a woody envelope and the endosperm or almond. The endosperm is surrounded by thin and elastic membrane rich in protein and oil. Olive fruits are green, and they turn to pink, purple or black depending on their maturity [1]. The composition of the olive fruit depends on genetic, environmental and cultural parameters. During their growth (June-December) both their weight and composition change. The olive fruit is consisted of water which reaches up to the 50-60% of the weight of the fresh flesh, olive oil (15-30% of the weight of the fresh flesh), carbohydrates and polysaccharides (3-6% of the olive mass) which are water insoluble, phenolics, flavonoids, proteins, pectins, organic acids, rosin substances, tannins and vitamins. The carbohydrates included in the olive fruit are glucose, fructose, mannose, galactose and sucrose, and polysaccharides, including cellulose, hemicelluloses and gums. The contained phenolics may differ concerning their solubility since some of them are soluble only in organic solutions and others may be water soluble or strongly insoluble isomers. All the phenolics are characterized by at least one phenyl group ($-C_6H_5$) bonded to a hydroxy group ($-OH$). Flavonoids are plant phenolic derivatives and luteolin, apigenin and rutin have been found in the olive fruit. The concentration of the fruits in proteins depends on maturity of the fruit. The olive oil is consisted of 70-80% monounsaturated fatty acids (oleic acid), 6-16% ω-6, 0.3-1.3% ω-3 fatty acids and 8-10% saturated fatty acids. The oleic acid has been found to increase the "beneficial" high number of lipoproteins (HDL) while reducing the oxidation of "catastrophic" low-density lipoproteins (LDL), thus helps in reducing of atherosclerotic activity. Moreover, the olive oil contains 64-86% of oleic acid, PUFAs, sterols (mainly β-sitosterol) triterpine alcohols, hydrocarbons and β-carotene and it is a source of vitamin E (virgin olive oil contains 100-140μg of tocopherol/g of oil) which is an excellent antioxidant [2,3].

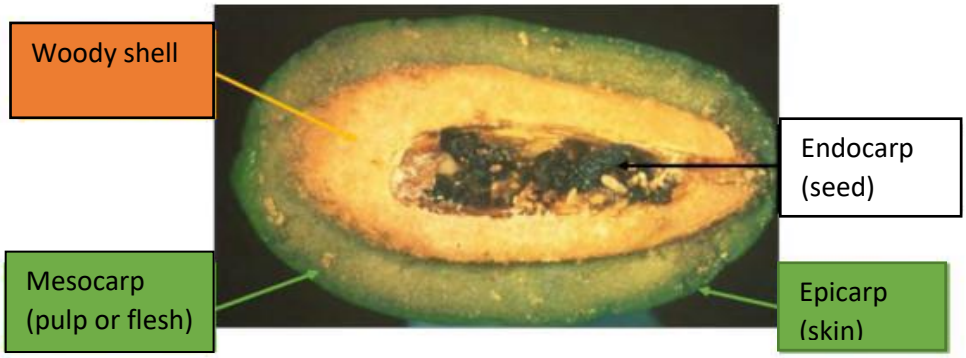

Figure 1. Olive fruit.

On the other hand, the production of olives is followed by a large amount of wastes which are phytotoxic due to the high organic load [4]. In modern olive mills, olive oil production is mainly based on the basic principles of pressure (traditional or classic systems) and centrifugation (continuous systems). The centrifugation systems are divided into three phases and two phases systems; Selective filtering, chemical separation and removal of crushed stones. The most commonly used methods are centrifugation and the traditional method of pressure. In pressure systems and in 3-phase centrifugal systems, the waste is both liquid and solid (named as Olive Mill Wastewater, OMMW) whereas in the 2-phase systems the resulting waste is a semi- solid wet pomace (or alperujo)[5,6]. Few years ago, the 2-phase mills were introduced as a more ecological system because they use less water and produce less quantities of liquid wastes. It should be noted that at the three-stage centrifugal mills, a large amount of water is added in the decanter for the extraction of olive oil from the olive pulp. At the two-phase olive oil mills, the centrifugal system separates the olive pulp after the stage of malaxation into two parts: the olive oil and the olive-pomace in which the wastewater is included in the form of a ~65 % moisture. The most important advantage of the system is the reduced water consumption and the diminishment of wastewater amounts. However, the problem of waste management is shifted from handling the liquids within the premises of olive mill to the treatment of semi-solid waste in huge pomace oil companies. Those companies must dry first the semi-solid waste before the extraction of the trapped olive oil in the kernels in the form of kernel olive oil. It is estimated that for each kilogram of processed olives, 800 kg of liquid olive-pomace are produced with concentration 80 g COD/L which corresponds to the annual polluting load of 22 million of people [7]. Moreover, the resulting crushed olive kernels are characterized by increased moisture and it is difficult to handle, transport and process.

Today, the interest of researchers has been focused on the treatment of solid waste from two-phase mills as it is produced in huge quantities with high polluting load. For example, in

Spain, where almost 90% of the oil mills have two-phase decanters, about 4.000.000 tons of semi-solid wastes are produced every year. Several methods have been developed for the treatment of olive mill wastewaters (use of membranes, membrane bioreactors, vacuum distillation) [8,9,10]. At the same time, scientists are also focused on the recovery of high added value by-products during the treatment of olive mill wastewaters such as phenolics which could be exploited commercially [11-14].

In the present work, an investigation of the phenolic recovery from the olive pulp is conducted. A parametric analysis has been performed, in order to find the optimum parameters for the recovery of phenolics from the olive pulp. Parameters such as the ratio of solid mass to water volume, the stirring duration and rate as well as the temperature during the extraction were investigated. Next, evaporation on the extracted solution was performed. The solution obtained from the evaporation was condensed using rotary evaporation and the phenolic substances were finally obtained in the form of powder after freeze drying. Finally, a novel scheme for olive mill has been designed with almost zero wastes, whereas the recovery of phenolics and other by-products could be exploited commercially.

METHODS AND MATERIALS

The extraction experiments were performed using a jar test apparatus (Flocculator "FLOC-6" RAYPA®). A parametric study for the optimum parameters for phenolics recovery was performed. In order to obtain the optimum conditions for the recovery of phenolics the following parameters were investigated: ratio of mass of semi-solid material to water volume, the stirring duration and rate and the temperature. For the investigation of the optimum ratio of solid mass to the volume of water, 10 gr of pulp were added in five different vessels and the distilled water volume ranged between 100-300mL. The extraction took place under 100rpm of stirring for 30 min. For the investigation of the optimum extraction time, 20g of olive pulp were added in 200mL of water in four different vessels. The duration of the extraction ranged between 15 and 60 min and the stirring rate was kept constant and equal to 100rpm. For the investigation of the optimum stirring rate, extraction experiments were conducted for stirring rate values in the range 50 and 200 rpm. The temperature effect on the phenolic extraction was investigated in the range of 25 to 55 ºC. The measurement of phenolics was performed using Folin-Ciocalteu method [9]. The used methods for carbohydrates and COD measurement are described in [9].

The phenolic recovery was performed using initially the above described extraction process followed by and vacuum distillation. After the extraction, a rotary evaporator was used (0.01 bar and 50 °C) to remove most of the solvent and to concentrate the extracts. The extraction was performed using 100g of pulp in 1L of distilled water for 60 min under stirring

at 150 rpm and at ambient temperatures. 50mL of the extracted solution were collected for measurements whereas 50mL of the initial water volume was remained within the olive pulp as moisture. The rest of the solution, that is the remaining, 900mL of the extracted solution were distilled for 90 min using a rotary evaporator (0.01 bar and 50°C). The concentrated solution which was obtained from the evaporator was only 25mL and this was further treated in a freeze-drying devise (Lyo Quest laboratory freeze dryer). The freeze-drying duration was 24 hrs at -77.2°C and under 0.513 mbar. Finally, 0.95 g of powder were selected. For the measurement of phenolics, carbohydrates and COD at the phenolics powder, the obtained solid was diluted in 2L of 3D water.

RESULTS AND DISCUSSION

Ratio of mass solid to water volume

The optimum ratio of semi-solid mass to the volume of the solvent (water) for the extraction of phenolics was investigated in the beginning of the experimental series. In all experiments 10 gr of semi-soli paste were used at different volumes of the solvent. In Figure 2 the concentration of phenolics and carbohydrates as well as COD values are depicted as function of the used water volume. The values in y-axis were normalized to show the recovered grams of phenolics or carbohydrates per kilogram of olive fruits (not semi-solid paste). Figure 2 shows that an increase is observed for COD values and carbohydrates concentration, while only a slight increase is observed for the concentration of phenolics when the volume of water is increased from 100mL to 150 mL. The COD and of carbohydrates values are decreased for higher water volumes. The concentration of phenolics is maximized for 200 mL of water. Because the main target is to get as much as possible phenolic compounds and the minimum possible values of carbohydrates, the dissolution of 10 gr of solids in 200 mL of water was considered as the optimum condition (ratio 1:20).

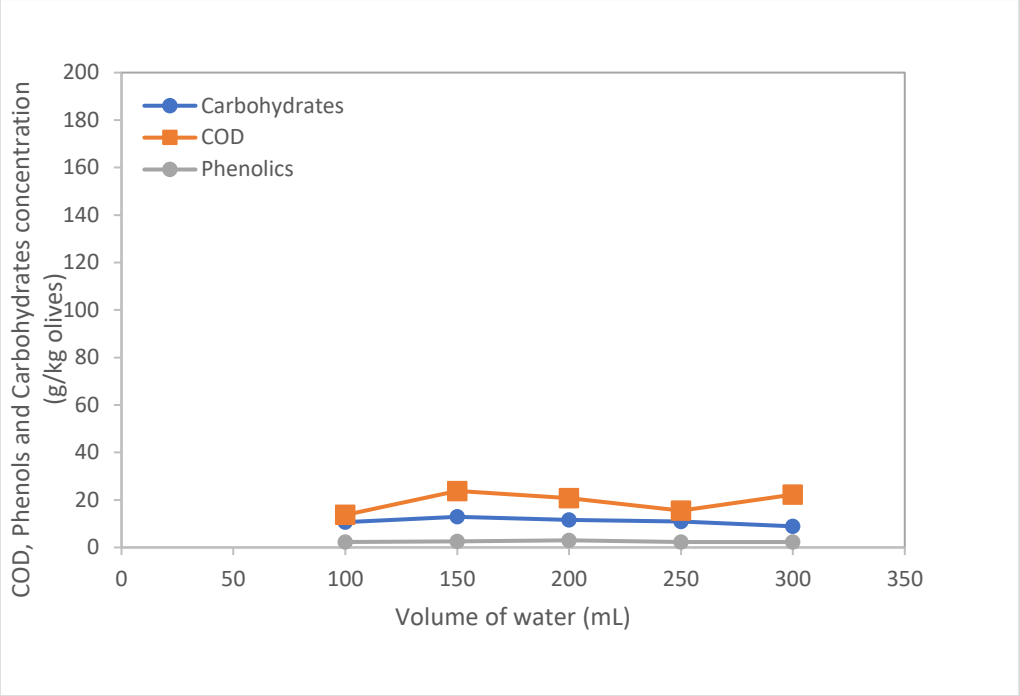

Figure 2. Phenols, Carbohydrates and COD concentrations as a function of volume of water used during the extraction of 10g olive pulp.

Figure 3 shows photos of the samples measured and as expected the color is less intense in large dilutions, because the concentration of organics is decreased.

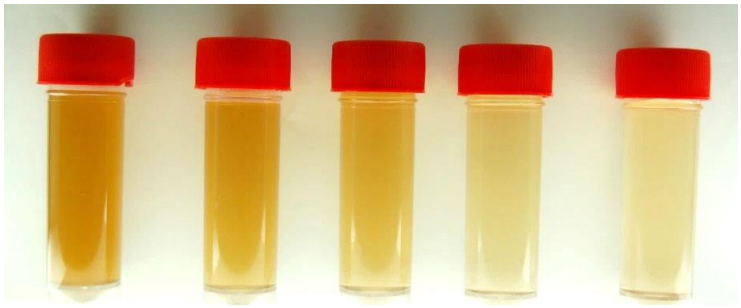

Figure 3. Samples obtained during the extraction of 10g of olive pulp using 100, 150, 200, 250 and 300 mL of water correspondingly (from left to the right).

Stirring duration

At this stage, the optimum duration of stirring for the extraction of phenolics was investigated. 20g of olive pulp were added in the jar test vessels and 200 mL of water were added as well. The samples were stirred for 15, 30, 45 and 60 minutes at 100rpm. The concentrations of phenolics and carbohydrates as well as the COD were measured, and the obtained data are

summarized in Figure 4. Carbohydrates concentration remains almost unaffected by the duration of stirring whereas phenolic recovery presents a short peak at 45 minutes of stirring. COD increases with increasing the duration of stirring, because other organics than phenols and carbohydrates were released in the solution. Figure 4 shows that 60 min is the optimum time for stirring for the range of time durations that were tested, which is also depicted at the colors of the extracted solutions shown in Figure 5.

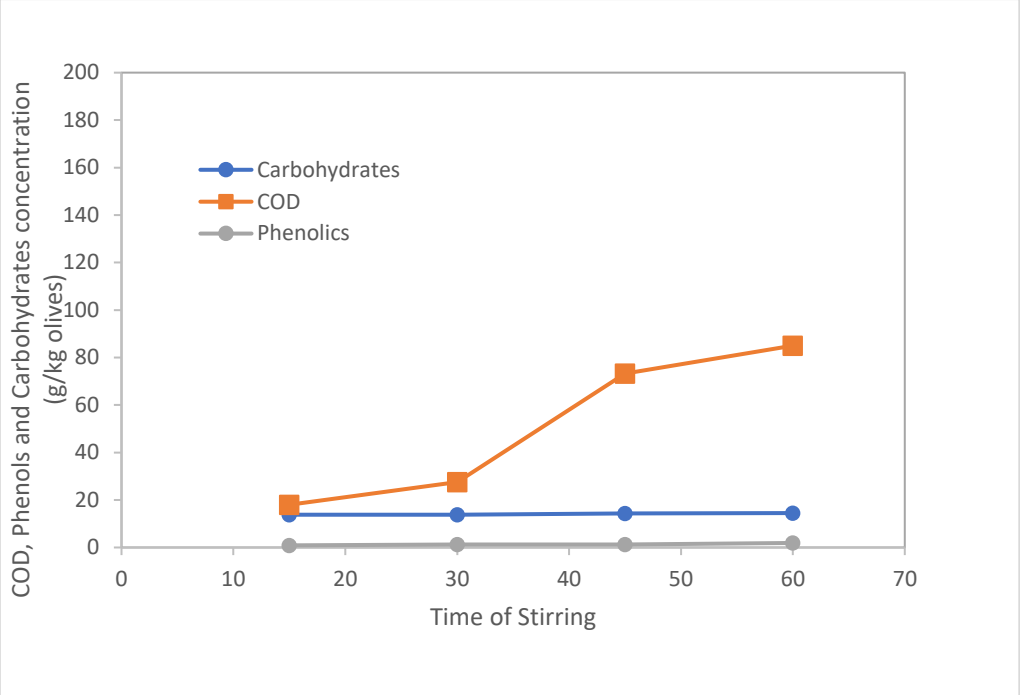

Figure 4. Concentrations of phenols and carbohydrates and COD as function of stirring duration used for the extraction of 20g of olive pulp in 200mL of water.

Figure 5. Extracted solutions obtained during the extraction of 20g of olive pulp in 200mL of water for stirring duration 15, 30, 45 and 60 minutes correspondingly.

Stirring rate

Next, the stirring rate was investigated in order to find the optimum rate for the extraction of phenols. 20g of olive pulp were extracted using 200mL of distilled water for stirring rates ranging between 50 and 200rpm. The COD and the concentrations of phenolics and carbohydrates which were obtained are summarized in Figure 6. It is observed that the higher concentration of phenols in the extracted solution was found for the extraction that was performed at 150rpm. However, the differences in phenolic concentration are not high and this is also depicted by the colors of the extracted samples in Figure 7.

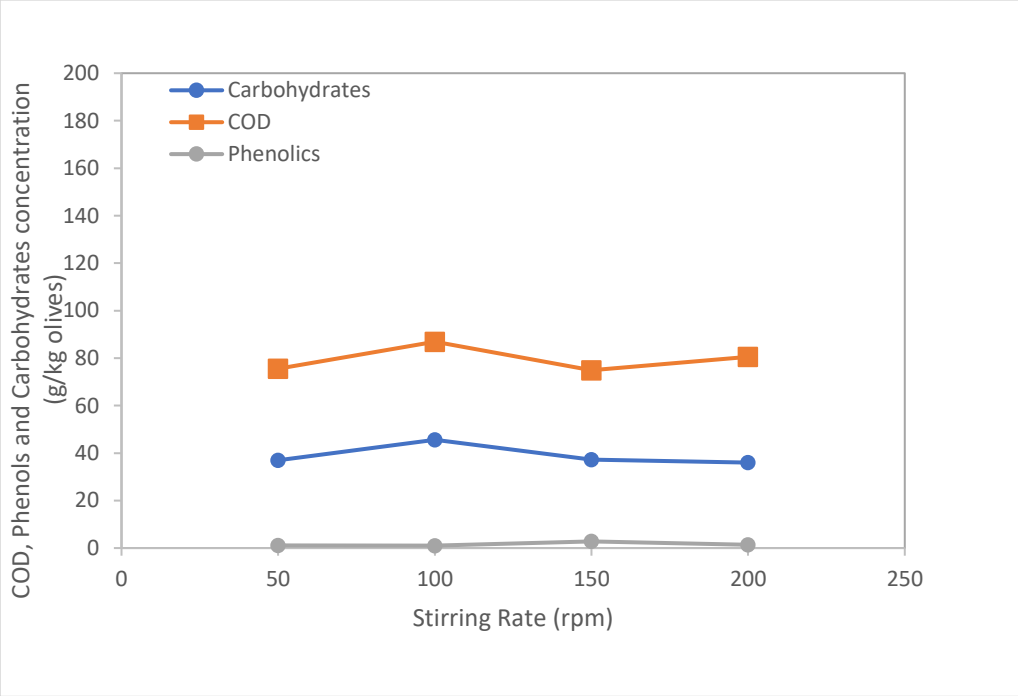

Figure 6. Concentrations of phenolics, carbohydrates and COD obtained from the extraction of 20g of olive pulp using 200mL of distilled water at 150 rpm for stirring rates ranging between 50 and 200rpm.

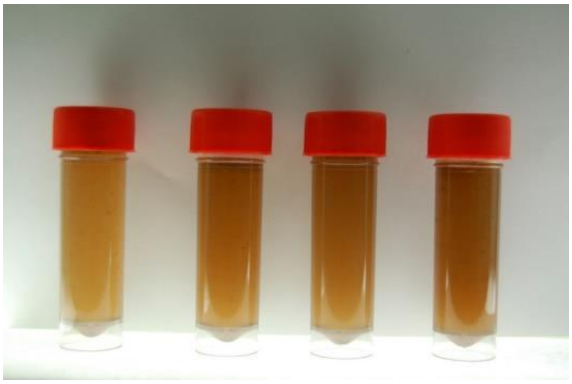

Figure 7. Samples obtained from the extraction of 20g of olive pulp using 200mL of distilled water at 150 rpm for stirring rates ranging between 50, 100, 150 and 200rpm correspondingly.

Temperature

In order to investigate the effect of temperature on the phenolics extraction, 20g of solids were extracted using 200mL of water at 150 rpm for the temperature ranging between 25-55ºC. The COD and the carbohydrates and phenols concentrations which were obtained are summarized in Figure 8. It is shown that the concentration of phenolics is increased at 45 and 55 ºC which is also shown by the colours of the extracted solutions presented in Figure 9. The value at 45 ºC were selected as optimum since when temperature approaches 55 ºC, the critical point of phenolics decomposition (~60 ºC) is close and this should be avoided.

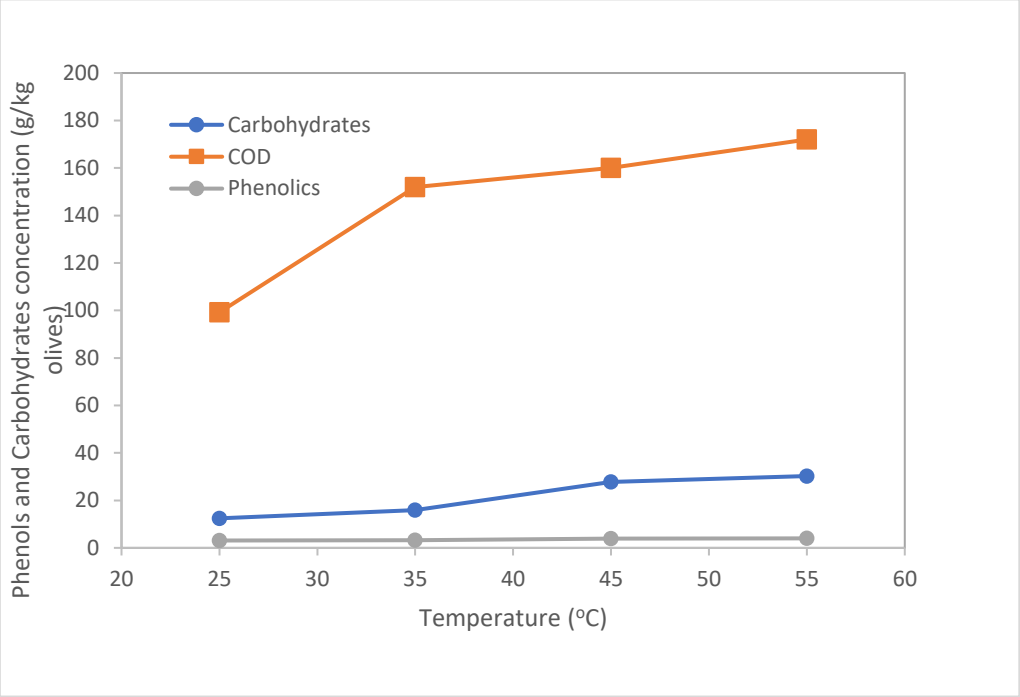

Figure 8. Concentrations of carbohydrates, phenolics and COD as function of temperature for the range 25-60 ºC.

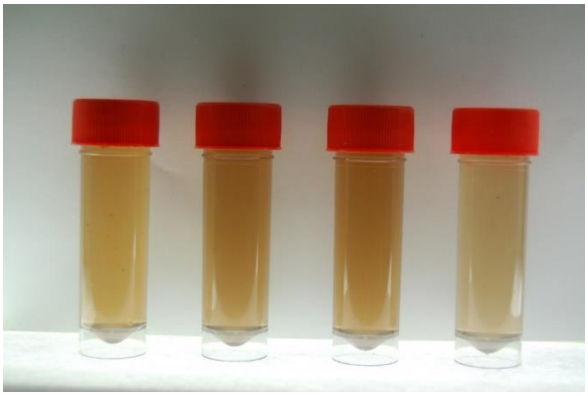

Figure 9. Samples obtained from the extraction of 20g of olive pulp using 200mL of water at 150 rpm for the 25, 35, 45 and 55ºC correspondingly.

Condensation of phenolics

100g of olive pulp were extracted in 1000mL of distilled water for 60 minutes at 150rpm at room temperature. 50mL of sample was collected at the end of the extraction for analysis of the extracted solution. Almost 50 mL of the solvent were found to be absorbed on the semi-solid paste and couldn't be removed. Thus, the supernatant solution of 900 ml was further treated in a rotary evaporator at pressure values close to 0.1 bar and 50 °C, for 90 minutes. Finally, 875 mL were evaporated and only 25 mL of concentrated solution were obtained as the bottom product (Figure 10). The concentration of phenolics in the initially extracted solution (Figure 10 (a) was found equal to 0.524 gr/L which could be attributed to 3.9g of phenols per kilogram of olives. At the distillate (Figure 10 (b)) the concentration of phenols was found equal to zero whereas in the concentrate (Figure 10 (c)) was found equal to **19** gr/L which can be attributed to 3.8g of phenols per kilogram of olives. The results show that the extracted phenolics were successfully condensed.

Figure 10. Samples from the (a) extracted, (b) distillate and (c) concentrate solutions.

The bottom product of a volume of 25mL of the concentrate solution was placed in the freeze-drying device for 24 hours and the final obtained powder was 0.95 g of solids (Figure 11). The concentration of phenolics and carbohydrates which were measured after the dilution of the final solid in 2L of 3D water were found equal to 0.1 and 0.2 g, respectively. Finally, high performance liquid chromatography measurements were conducted and the presence of oleuroid, hydroxytyrosol, gallic acid and for rutin was detected.

Figure 11. Phenolics obtained in the form of powder after the freeze drying of the concentrate.

DESIGN OF AN INNOVATIVE MILL

At this stage, the design of an innovative mill, with environmentally friendly processes and the elimination of wastewaters, was performed. The new process includes 5 basic stages (Figure 12): The first stage (brown color) concerns the separation of pulp from the stones. The second stage (black) is the pellet pickup process. The third stage (red) is the extraction of water-soluble phenols from the pulp. The fourth stage (blue) is the recovery of phenolics in the form of powder using freeze drying. Finally, the fifth stage is the production of olive oil from the pre-processed pulp with the existing two-phase production process. More specifically, initially the olives are picked up, weighed and transported to the de-shelf. Then, they are fed to the deflector where the leaves are separated from the olives. The removal of the leaves is very important, because their crushing gives to the olive oil a bitter taste. Then, the olives are left in the washing machine. The washing machine includes a water tank, a water pump, an air blower and a rotating water filter. The pump circulates the water in the bowl, creating a flow of water and in combination with the air that is fed by the blower, the olives are stirred for the removal of impurities. A plastic film, located at the exit of the washing machine, carries the olives into the hopper of the pulp-crucible separator machine [15]. The stones are transferred to the shredder while leaves and solids from the washing machine are transferred for processing to the pelleting machine [16]. The pulp which has been separated from the stones is then conveyed with a strap for extraction and the pulp is stirred. Finally, the extract passes through vacuum filtration filters. The water proceeds with a pressure pump on the distillation column and the pulp is leaded to the softener. The water which comes from the extraction, proceeds with a pressure pump to distillation in order the phenolic substances to be recovered. The condensate from the distillation is directed for freeze-drying and finally the phenolic substances are collected in the form of powder. The malaxation of pulps speeds up the joining of small oil droplets into larger drops and the olive oil is produced. The separation of olive oil is carried out in the decanter. Then, the water and the olive oil pass through a vibrating filter where the remaining solids are

removed, and the unused pulp is transferred to a suitable container in order to be treated for animal feed. The pulp is free of stones which gave the high organic and phenolic content and made it unsuitable for animal feed. The olive oil is then pumped to the oil separator for further purification and it is finally collected in containers. The water is pumped to the disposal site together with the remaining of the process for filtration and reuse. Olive oil is received with plastic containers from the olive growers. All the water used during is filtered and returned for further use such as machine cleaning.

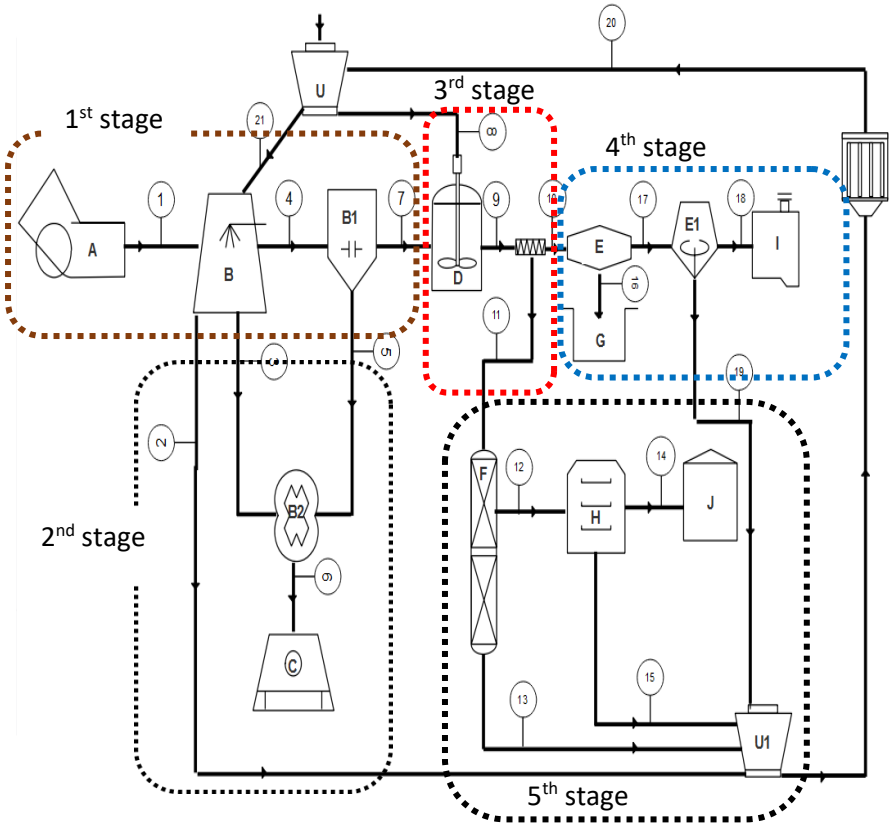

Figure 12. Scheme of the innovative mill. A. Olive supplier?, B. Washing machine, B1. Stone separator, B2. Shredder, C. Pellet constructor, D. Extractor, E. softener, E1. Separator of water and oil, F. Distillation column, G. Pulp reservoir, H. Freeze dryer, I. Oil reservoir, J. Reservoir for phenolics, U. Water tower (water supply reservoir)

CONCLUSIONS

In the present study, a parametric investigation of the phenolic recovery from the olive pulp was performed. The optimum ratio of semi-solid mass to solvent volume (water), the stirring rate and duration and the temperature effect were investigated. The extracted solution was distilled and condensed using a rotary evaporator. Finally, it was dried in a freeze-drying device

and the phenolic substances were obtained in the form of powder. High performance liquid chromatography on the diluted powder in 3D water showed the presence of oleuroid, hydroxytyrosol, gallic acid and rutin. Finally, an innovative mill with eliminated wastes was designed. The olive oil production process included five stages; (a) the stone extraction from the olives, (b) the pellet pickup process which will be used for animal feed, (c) the extraction of water-soluble phenols from the pulp, (d) phenolics recovery after freeze drying and (e) olive oil production from the pre-processed pulp using the existing two-phase production process. According to this design, there are no wastes during olive oil production, the water is recirculated, and it can be used for the needs of the mill (such as machine cleaning) and the phenolics substances which are recovered may be exploited commercially.

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