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Research Paper

Separation and purification of high purity products from three different olive mill wastewater samples

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ABSTRACT

Morocco is known for producing olive oil, which release olive mill wastewater (OMW) on rates that are growing exponentially. This resulting effluent produced through discontinuous (traditional units) or continuous processes (modern and semi-modern units) is qualified as a highly polluting substance, since it contains great concentrations of chemical and biological oxygen demand and contains high concentration of organic substances. Despite its treatment throughout the extraction process, this liquid waste still contains a very important oily residue, always considered as a pollutant waste.

This research is one of the first studies describing a new method to treat and value the OMW as well as to extract new eventual products. The proposed pre-treatment process consisted in a centrifugation in which the remaining oil from three OMW samples (press, two and three-phase centrifugation system) was recovered, the inclusion with urea came out with oleic and linoleic acid with high purities, the triglycerides forming this oily part were transformed into methyl esters, and then crystallized four times with urea at (4 °C and 20 °C) for methyl oleate and (−5 °C) for methyl linoleate, also biodegradable soap and extra pure glycerol were obtained with high qualities from the same phase. Furthermore, the aqueous phase resulting from centrifugation has been treated with ethyl acetate to recover the polyphenolic compounds with a yield of 67%.

With this new procedure followed in the present study, from one liter of OMW's oil it seems possible to obtain 137 g of purified oleic acid and 37 g linoleic acid.

In order to ensure both, feasibility and economic viability of the OMW treatment project, a case study was performed based on Marrakesh region data. The prototype of the unit yield favorable results.

1. Introduction

An acerbic concern was devoted to treat olive mill wastewater OMW, mainly due to high organic fraction, including sugars, tannins, phenolic compounds, polyalcohols, pectins and lipids [1,2], that present an increasing environmental hazard.

Dozens of methods have been tested for detoxification of OMW: Physical and chemical processes such as: lagooning [3], composting [4], fertilizing [5], biogas production [6], coagulation-floculation [7], electrocoagulation [8], adsorption [9,10], and filtration [11]. Thermic treatment: evaporation [12], incineration [13], besides biological treatments: aerobic digestion [14] and anaerobie treatment [15].

Techniques were developed for antioxidants recovery [16,17] and other components such as dietary fiber suspensions [18], volatile fatty acids (VFAs) [19] and a lipase producing bacillus pumilus [20]. That said, there is something very important missing. Obviously, the oily part remaining in these effluents was neglected and not extracted even if it contains high fatty acids.

Oleic and linoleic acid are the most widely used fatty acids, they have received increased attention due to its versatility in many different fields, such that of biodiesel, textile, lubricant, cosmetics and nutritional additives [21–27]. It was always difficult to separate these two expensive products from other fatty acids and also between them, especially that they have the same characteristics.

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Different technologies have been developed to separate and purify these two components, such as liquid extraction [28,29], fractional distillation [30,31], inclusion with urea [32,33]. Except the last method, all such methods were abandoned due to higher operating costs, since they must always be followed by a complementary process.

The urea complexes, is a simple, effective and reliable technique for extracting pure fatty acids, with respect to yield and fatty acid composition in the concentrate. This method is based on the degree of unsaturation: the more unsaturated, the less they will be included in the urea crystals [34,35].

However, all these processes mentioned above were carried out from virgin oils, such as olive, safflower and seed oil, neglecting the richness of their wastes especially the olive mill wastewater.

In addition to fatty acids, the phenolic compounds are very abundant in the OMW and are the major responsible of its black color and polluting load. Not only are they crucial for the oil stability but also the source of its antioxidant properties [36]. Many factors are interfering on determination of their concentration in oils factors: geographical origin, processing technique, storage time, and irrigation system [37].

A particular focus was devoted to separate phenolic compounds from OMW by using adsorption [38,39], integrated membrane processing [40,41], cloud Point Extraction [42,43], cooling crystallization [44], ultrafiltration [45], supercritical fluid extraction [46,47], liquid–liquid extraction [48,49]. The use of this last technique was preferred for its simplicity and convenience, it remains more advantageous not only because of its lower cost and its better yield, but also because it could be applied even in small, family-owned olive oil mills that exist in most Mediterranean countries, the case of Morocco [50].

The first objective of this study is to describe a new technique to extract and separate two polyunsaturate-free fatty acids, with high purity by a fractional crystallization with urea from OMW collected from three olive oil extraction processes (traditional, modern and semi modern). A comparative study was investigated with different OMW samples. By centrifugation, the oily phase would be extracted from OMW; which is destined to be a platform to obtain two fatty acids (oleic and linoleic acid).

The second objective is to ensure a total valorization of our effluent, a complementary process was carried out for production of a high quality soap, glycerol and polyphenols. The extraction methods, the isolation of oleic acid, and the production of soap and glycerol are performed the same way as the previous work of the same authors [51].

Finally, a pilot plant was designed and developed for a full olive harvesting period (100 days), in the one of the biggest olive production areas of Morocco (Marrakech-Safi), in order to carry out a socio-economic study, which consists in studying the feasibility of OMW valuation project for the three local olive oil extraction processes.

2. Materials and methods

2.1. Characteristics of olive mill wastewater

Olive mill wastewater was collected during the 2014 and 2015 production campaigns from three processing plants using different methods of trituration: a traditional press and a continuous process (two and three-phases system) located in Marrakech (South of Morocco). This region is one of the biggest olive production areas of Morocco. No chemical additives are being used during the olive oil production. The OMW solid particles were removed after settling and filtration.

A total of 20 l of OMW from each oil mill was stored in a closed plastic container of 5 liters and kept in a dark place at an approximate temperature of 20 °C. The main physical and chemical characteristics of the olive wastewater used in this study are listed in Table 1.

2.2. Separation

After the storage of the samples, the oily and aqueous phases of OMW can be separated either naturally or by centrifugation. Even if they have the same performance, but the slow and the area requirement may limit the first one.

The centrifugation allowed us to accelerate the separation of oil and water phase. This separation technique is performed by filling 4 test tubes with 250 ml of OMW solution, they are then centrifuged at a speed of 4000 rpm during 30 min using a centrifuger. The oil, having a lower density than water, will be found above the water in the centrifuger. In order to finally isolate the oil, it will be collected using an automatic adjustable pipette. Oil percentage was determined using weight difference.

2.3. Analytical methods

2.3.1. Acidity

By natural hydrolyzing, both free fatty acids (FFA) and glycerol rise. One of the best ways to determine the fats alteration following hydrolysis is the measurement of free acidity.

Acidity is the percentage of FFA expressed conventionally depending on the nature of the fat. Molecular weights of oleic acid, palmitic acid and lauric acid are 282, 256 and 200 respectively.

Except palm oil, whose acidity is expressed as palmitic acid and fats (coprah and palmiste), oleic acid is used for all fats.

For the determination of acidity (percentage of oleic acid), 10 g of separated oil from OMW were transferred into an Erlenmeyer flask containing previously 50 ml of ethanol 96%. These fatty acids are titrated with KOH solution (0.1 N) in the presence of phenolphthalein until a persistent pink color appears after about 15 s [52].

The acidity could be calculated as follows:

$$\text{Acidity (oleic acid) \%} = (N \times V \times M)/(10^{*}m) \quad (1)$$

Where

N: Normality of the KOH solution.

V: Volume in ml of titrated KOH solution used.

M:Molar mass of oleic acid: 282 g/mol.

m: Mass in grams of the test sample.

2.3.2. Peroxide index

Chemical alteration of the unsaturated fats by air's oxygen begins with the formation of peroxide. This reaction is autocatalytic. The principle of determining the peroxide value is based on the oxidation of iodide to iodine by active oxygen and titration of the liberated iodine with sodium thiosulfate.

Table 1
Some chemical/physical characteristics of olive mill wastewater obtained from traditional and modern units located in Marrakech, Morocco.

Type oil mill	Traditional (Press process)	Continuous Process (Two-phases)	Continuous Process (Three-phases)
pH	5,2	4.64	4.32
Conductivity (mS/cm)	10,15	13.66	11.25
Polyphenols (g/l)	2,1	1.95	3.15
Total Suspended Solid (g/l)	3,45	2.15	3.59
COD (g O_2/L)	28,15	22.35	24.49
BOD_5 (g O_2/L)	14,35	8.36	11.64
Oily fraction% (m/m)	37.05	26.25	10.8