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New Eco-friendly process tanning by concentrated recovered from Olive Oil Mill Wastewater

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Abstract

Olive Oil Mill Wastewater (OMW) is a serious environmental problem in Morocco, which is known for producing olive. OMW is characterized by a high organic load and the presence of high concentrations of organic substances (COD:67.2 g/L; BOD5: 70.6 g/L; CE: 11.5 mS/cm). The main objective of the present study was to optimise the conditions of treatment of olive mill wastewater. The waste was treated by solar energy to reduce quantity of OMW without affecting the environment. The concentrate containing 14% of phenol was obtained by this procedure of treatment and was applied aseco-leather tanning agent to replace chrome-tanning process who represent more than 85% of global leather production. Despite the polluting power of this tanning process and that toxicology reasons unfairly associating the chromium (**2**I) commonly used with hazardous chromium (VI). The characteristics of the leather indicate that the vegetable tanning system used in our study provides leather with a good physical and chemical property

Keywords: *Ceramic; zinc phosphate cement; orthopedic material; dental material; sintering; porosity, antibacterial test*

I. Introduction

Olive oil production is one of the most traditional agricultural industries with a great economic importance in Morocco. In terms of production, the olive sector produces 1.5 million / year [1]. This sector generates about 72.000 tons liquid waste; the solid waste called olive pomace estimated at 30.000 tons/year [2].The liquid effluent called olive-mill wastewater (OMW) is a major environmental problem. The traditional units of production are the most common and their OMW generally is rejected near the unit. The modern industries, which apply modern technologies, generate important quantities of OMW evacuated without preliminary treatment and that create disturbances of the natural ecosystems [3]. The OMW cause serious environmental pollution problems due to their high level of production and specific chemical characteristics. OMW is one of the strongest industrial effluents that is characterized by relatively acidic pH (4.5 – 5.5), high organic content Chemical Oxygen Demand COD values>90 g/L and biochemical oxygen demand “BOD” values >25 g/L that make the management difficult [4]. OMW contain lipids, sugars, polyalcohols, amino acids and polyphenols that contribute to the extremely high organic content of the OMW (40–165 g/L)[5]. Polyphenol is also responsible for the dark color, phytotoxic effects and antibacterial activity of the OMW [6]. Traditional methods used for treatment of OMW, disposal in shallow evaporation ponds, disposal in soil, incineration and utilization for the production of fermentation products [7]. Various researchers have proposed different methods for the treatment of OMW, such as evaporation ponds [8],chemical treatment [9], co-composting[10], land disposal [11], electrochemical treatment [12], adsorption [13, 14],and ultrafiltration[15]. Leather industry has been categorized as one of the highly polluting industries and there are concerns that leather-making activity can have adverse impact on the environment and health[16].Considered one of the eight world-wide professions in Morocco, the leather sector continues to represent one of the sectors with high export potential for the Moroccan industry[17].The tanning industries, in Morocco, are growing fast. Many new tanneries are opened. Chrome tanned leathers are commonly adopted tanning practice due to top handling quality, high hydro-thermal stability and excellent user properties.. However, chrome wastes from leather processing poses a significant disposal problem. It occurs in three forms: liquid waste, solid tanned waste and sludge. From the amount of chromium used for tanning only 60 and 65% are taken by the leather, the remaining 30 and 40% of the chromium salt used is discharged in the tanning effluent [18-20]. Based on our patent filed in 2006 [21], our research focused on the study of greenhouse evaporation of olive oil wastewater using solar energy to reduce the volume of waste liquids and obtain an OMW concentrate.Also, the overall objective of the study is to develop effective chrome free tanned upper leather based on vegetable tanning. Since the OMW is rich in tannin, which is a substance whose property is to form an insoluble compound and capable of rotting on collagen.

2. Material and Methods

2.1. The olive oil mill wastewater (OMW)

Olive mill wastewater was collected during the 2013 and 2014 production campaigns from processing plants using a traditional press located in Fes. This region is one of the biggest olive production areas of Morocco. A total of 250 L of OMW was stored in a closed plastic container of 50 L.The OMW was immediately analysed for determination pH, conductivity. After 4 weeks of the storage of OMW, the oily and aqueous phases of OMW are separated naturally.

2.2. Greenhouse

The solar distillatory used in this experimental study consisted of the liquid basin where the OMW was placed, the greenhouse uses solar radiation to warm the surface of the OMW and aeration to allow evaporation of the water, this one is thus evacuated by natural convection (figure 1). Experiment was conducted between 31 July and 30 august

2014 (duration: 28 days). Measurements of temperature (ambient fair, OMW), temperatures were measured using thermometer for three times and the average is recorded.The temperature range in greenhouse is mentioned in figure 2.

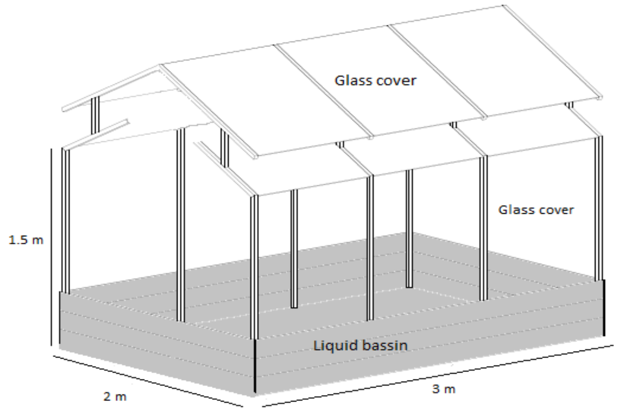

Figure 1: Three dimensional representation of the experimental greenhouse basin used in this study.

2.3. Analytical methods of OMW

The pH was measured using a pH-meter (Vantakool digital pH-meter) in a suspension of 10 mL of OMW at ambient temperature. The conductivity was determinate by conductivity-meter (HANNA Instruments EC215).The moisture was determined by a gravimetric method on a sample of 20 ml of OMW. The total suspended solids (TSS) was determined by centrifugation method of 50 mL of OMW during 20 min at 8000 rpm, the pellet is placed in porcelain crucible previously weighed and then dried at 105°C for 24 hours. The difference of weight after drying determines the rate of TSS [22]. Total volatile solids (TVS) was carried out according to standard methods by distinguishing between the dry matter obtained by evaporation at 105°C and the residues of ash resulting from the calcination of the dry matter at 550°C for 5 hours [23]. Concentrations of the chemical oxygen demand (COD) was measured using the open reflux method in accordance with the standard methods for the examination of water and wastewater [23,24].The biological oxygen demand (BOD_5) signifies the biodegradable fraction of organic matter in OMW, involving bacteria and fungi. The diluted samples were incubated in a BOD-meter, which gives the amount of oxygen consumed by the microorganisms for 5 days at 20°C in the duskiness [25].The determination of the phenolic compounds was carried out by colorimetric method using the reagent Folin-Ciocalteu[26]. All analysis was repeated three times, the reported results are averaged.

2.4. Method tanning experiments

Two types of skin were used for this study, calfskin and sheepskin. They were recovered from the slaughterhouse located at Rabat city. The preparation of skin for tanning, contain a sequence of operations to remove parts of the skin not used in the processing of leather, that is to removal the epidermis, hair and subcutaneous tissue. After preparing the skin, we processed directly to tanning in basins containing the concentrate of OMW dilute twice and the skin was rotated twice a day. Furthermore, a new suspension as previously mixed with 3 % of animal oil to improve the physical qualities of leather.

2.5. Physicochemical analysis of leather

The physicochemical analysis was carried out for experimental leathers according to the standard procedures [27]. The moisture content was determined by drying 5 g of leather sample in an air oven at 105°C for a period of 3 hours. Ash content was measured by the gravimetric method of sample in an oven at 800°C until the constant weight was achieved. The fat content was performed by solvent extraction method of 5 g putting via asoxhlet extraction for 5 hours using dichloromethane solvent; the fat content was estimated as percentage (w/w) with respect to the input

sample. The chromic oxide content was obtained by the absorbance spectrophotometrically method at 372 nm. Analyses were carried out in triplicate and the average values are reported.

3. Results and discussion

3.1. Characterization of OMW

3.1.1. Physicochemical characterization

The OMW present a highly polluted rejection in the form of residual liquid whose composition is variable. Since the physicochemical proprieties of OMW depend on local and seasonal factors : the type of olives, the degree of maturation, the cultivation systems and the process used for extracting olive oil [28].The main characteristic properties of the OMW samples are given in Table 1.

Table 1: Properties of olive oil mill wastewater (OMW) used in the experiment

Characteristics	Results
pH	4.6
EC (mS/cm)	11.5
Moisture (%)	88
Total Suspended Solids TSS (g/l)	13.9
Total Volatile Solids TVS (g/l)	67.6
Total Solids TS (g/l)	76
Chemica Oxygen Demand COD (mg of O_2/L)	35.16
Biological Oxygen Demand BOD_5 (mg of O_2/L)	15.82
BOD_5/COD	0.45
Phenolic compounds (g/L)	1.5

The OMW represent a brown to reddish-brown coloration, which becomes darker during storage with a cloudy appearance and a strong smell that reminds one of olive oil. This dark color corresponds with the high amount of solids and phenolic compounds. The OMW is generally acid with values between 4.5 and 5.32[3,29]. That is confirmed by our study with the value of 4.6. The acidity of OWM can be explained by autooxidation and polymerization reactions, which transform phenolic alcohols into phenolic acids [3,30]. These reactions are revealed by a change in the initial colour of the OMW to a very dark colour [30]. Wastewater contains high salt content. Salinity is usually described in electric conductivity [31].The OMW studied had an average electrical conductivity of about 11.5 mS/cm, far exceeding the permissible effluent limit (7.00 mS/cm). The electric conductivity value of OMW in our study is comparable to that found in the literature, which varies between 9.6 and 12.5 [32,33]. The average contents of OMW in dry matter and total suspended solids are respectively 76 g/L and 67.6 g/L. the volatile matter present 89% of the dry matter, which shows the organic nature of these effluents. These values is close to that observed by several authors [29,34,35].

3.1.2. Environmental characterization

The OMW are an important pollution factor because they contain an important organic fraction (proteins, lipids, polyphenols, and carbohydrate) and their high total solids content [36]. The OMW are rich in organic matter expressed

in terms of BOD_5 and COD. From the table 1, the values obtained are 35.16 g/L for COD and 15.82 g/L for BOD_5. The obtained values are comparable to those obtained with several authors [29,30]. Both pollution parameters COD and BOD_5 allows to confirm a good approach about biodegradability. The BOD_5/COD report equal 0.45 which shows that the effluent is readily biodegradable cause the $BOD_5/COD > 0.33$. The OMW are also characterized by the presence of toxic substances including phenolic compounds with a content of 1.5 g/L. These results are confirmed by data from the literature [37]. According to several authors, phenolic compounds have an antimicrobial power, which limits any natural biodegradation [38,39].

3.2. Evaporation process

The proportion of water present in the OMW decreased strongly during the two first weeks in the greenhouse, the level decreased to -24 cm (figure 2). The evaporation was significant due of the removal of the oily surface during storage.At the end of the experiments, the volume of effluent was reduced 7 times, which proves the high efficiency of this technique in order to eliminate effluents that are harmful to the environment.

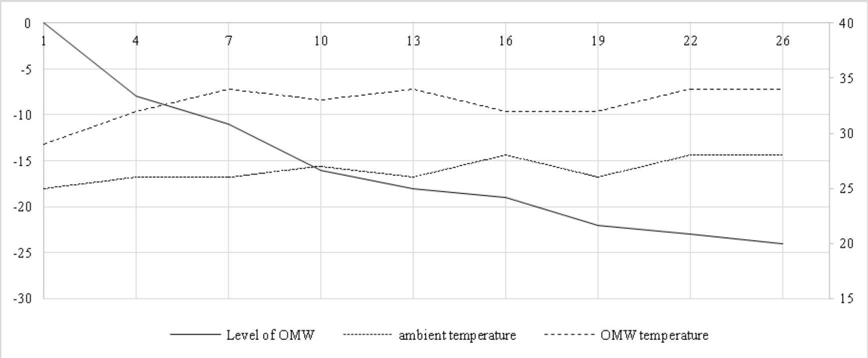

Figure2: Variation of ambient temperature, OMW temperature and evolution of the evaporation of OMW

The Figure 2 shows the fluctuations of measured temperatures during evaporation. The temperature difference between the ambient air and the olive oil mill wastewater is almost 6°C. A concentrate of the OMW was recovered after 26 days of the evaporation and is characterized by a high concentration of phenol. This result has oriented our study towards the valorisation of this concentrate in tanning of the leather.

3.3. Vegetable tanning

Tanning is chemical process by which additional crosslinks are introduced into collagen, binding active groups of tanning agents to functional groups of protein. There are many factors governing the tanning effect: the type of the tanning agent, concentration of tannins, pH value, and neutral salt content; the temperature of the tanning bath; and the residence time, the previous condition of the skin material is also important. Leather processing involves a series of operations. Many of these factors are interdependent and difficult to consider separately. A concentrate of OMW with 14% of tannin has been prepared as an attempt to widen the options for alternative tanning system, to combat chrome pollution. In the present investigation, the using of the concentrate of OMW is expected to improve the leather properties as well as abate chrome pollution.

3.4. Physicochemical characterization

The final appearance of the leather after tanning shows that the various leather are brown with a flexible handling, low elasticity and they resist to warm up despite friction (Table 2).

Table2: Physicochemical analysis of leather with vegetable tanning

	Physical appearance	Density (g/m^2)	Moisture (%)	Ash content (%)	Fat content (%)	Chromic Oxide (%)
Calfskin	- Brown color, -Flexible handling, -Low elasticity.	0.268	20.80	6.4	11.1	0
Re-tannedcalfskin		0.272	19.63	6.1	12.1	0
Sheepskin		0.158	18.34	5.7	10.7	0

The prepared leathers were tested in Leather Specialized Institute in Casablanca city. The results indicate a better physicochemical property. The general appearance, color and roundness of leathers tanned by concentrate of OMW as shown in fig. 2 are compared to leather chrome tanned. The results for the experimental leather are comparable to other tanning trials using plants in several scientific experience [36,40,41]. We not that the results are comparable between the different skins used in this study (table 2). The study indicate that vegetable tanning using concentrate of OMW can be easily adopted in the tanneries in Morocco. Their use will reduce imports of chrome and will lessen the attendant pollution.

Figure 3: Leather tanned with concentrate of OMW

Conclusion

The sample of the olive oil mill wastewater collected have very complex physicochemical composition. In this study, we shown the use of solar energy can resulted to OMW dewatering in a period of 30 days and to the production of concentrate of OMW containing a high rate of tannin, which we applied as a leather-tanning agent. The results of the experience clearly suggests that chrome tanning system can be replaced by concentrate of OMW tanning system so that the risky environmental impacts caused by the chromium compounds can be eliminated. The evaporation with solar energy seems to be a promising, low-cost, eco-friendly process for OMW treatment. Further research should be conducted to optimize the process of the evaporation. The application of OMW concentrate as leather tanning agent can be improve by adding other non-polluting agents that can give a superior quality to leathers.

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