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Research Article

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Evaluation by a principal component analysis of physico-chemical parameters of oil mill wastewater (OMW) in four regions of Meknes-Tafilalt

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ABSTRACT

The purpose of this study was to evaluate the physico -chemical quality of oil mill wastewater (OMW) in four different regions of Morocco (Oued Jdida El Mhaya, Route de Rabat and Sidi Bouzekri).A comparative study has been studied with several samples of OMW from two processes of extraction of olive oil (semi- modern and continuous). The results of the physicochemical analyzes showed that the four regions has an acidic pH which is the average value of 5,478 + 0,254 and the conductivity values vary between : 4,620 and 11,500 (mS/cm). They are rich in organic matter. This parameter is expressed by the COD and BOD_5 of which the average of all samples respectively is (39.095+17.397 gO_2/L) and (101,033 + 33,122 gO_2/ L, the acid is (1,402 + 0,197). The statistical study gave us the variance percentages 45,44 % to 30,77% for F1 and F2 whose total information is estimated at a percentage of 76,22%. Cartesian diagram enabled us to identify four groups and confirm that the station ***S1*** *is the most polluted of the four sites studied.*

Keywords*:* Oil mill wastewater; physicochemical parameters; Meknes-Tafilat region; Picholine ; Principal Component Analysis.

INTRODUCTION

The oil mill wastewater reddish-brown color with black olive pits and pulp. This residue causes serious environmental problems in all Mediterranean countries to olive growing (pollution of rivers,groundwater, ...) whose solution represents a real challenge upstream and downstream of the olive oil sector [1] .

The constitution of the by-product of the olive tree (oil mill wastewater) and their characteristics depend largely on the extraction systems used : Three -phase or two phases.

The three-phase continuous extraction system uses a lot of water and generates large quantities of liquid waste (oil mill wastewater) pollutants compared with the two-phase system which requires less water [2] .The quantity of the oil mill wastewater produced vary based on the trituration systems used, for the system with press the quantity of oil mill wastewater is produced from 450 to 650 liters / ton of olives, however for the three-phase system it is 850 to 1200 liters / ton of olives.

The Principal Component Analysis PCA is a widely used method in the field of water, also more common in wastewater applied to supervise the treatment processes of several years [3,4,5]. Through the data collected directly in the process, the PCA provides graphical tools easy to be analyzed and explained by operators and finally make an empirical model used to reference process behavior.

Indeed, the application of different multivariate approaches (cluster analysis (PCA), principal components analysis, source apportionment by multiple regression on principal components) for the interpretation of these complex data

matrices offers a better understanding of water quality and ecological status of the studied systems, allows the identification of the possible factors/sources that influence the water systems and offers a valuable tool for reliable management of water resources as well as rapid solutions on pollution problems [5,6].

This work aims to characterize the Oil Mill wastewater (OMW) of the Meknes region by their physicochemical quality and study the terroir effect on these parameters. The work was carried out on samples of (OMW) selected in the following areas: Oued Jdida (**S1)**, El Mhaya (**S2)**, Route de Rabat (**S3**) and Sidi Bouzekri (**S4**).

EXPERIMENTAL SECTION

Study sites

The samples were obtained from four oil mills located in the Meknès-Tafilalt region of Morocco (Oued El Jdida Mhaya, Route de Rabat and Sidi Bouzekri), between Novembre and March during the Olive period of the year 2014 - 2015 (Table 1 and Figure 1).

Samples have been taken from oil mills storage tanks the process works by a press system and three-phase. The analytical results and their interpretation depend essentially on the method of sampling, conditioning and storage time.

For this, our samples were collected in clean containers rinsed several times with the Oil Mill wastewater (OMW) to be analyzed then hermetically closed without leaving air bubbles in the vial. Then transported to the laboratory as soon as possible to keep it at 4° C for physicochemical analysis.

Table 1 : Different type samples of olive oil mill wastewaters obtained from the region Meknès -Tafilalt in Morocco

Symbol	Type oil mill	Study site
S1 : Station 1	Press system	Oued Jdida
S2 : Station 2	Press system	El Mhaya
S3 : Station 3	System has three phases	Route de Rabat
S4 : Station 4	System has three phases	Sidi Bouzekri

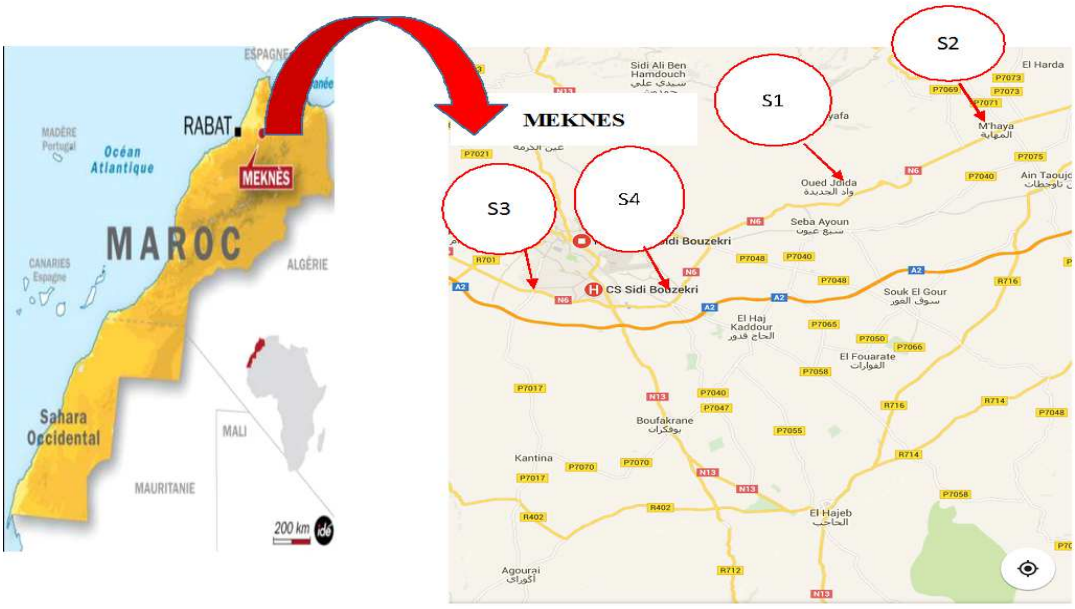

Figure 1 : Location of the unity of trituration in the Meknès -Tafilalt in Morocco

Statistical analysis

Data processing and multivariate statistical method of all quantitative analyzes of the water has been treated by multivariate statistical study XSLAT software to study changes in water quality. For this we performed a multivariate analysis, Principal Component Analysis (PCA) [7].

Physicochemical analysis of OMW

The measurement of pH, electrical conductivity and salinity were made by a multi-parameter analyzer type Consort C535 and Hanna Instruments HI 98280.

All physicochemical methods were standard methods [8]. Total suspended solids (TSS) was determined by weight difference of a filter membrane (d=0.45lm) before and after filtration. Chlorides and organic matter were determined by the Mohr method and oxidation by potassium permanganate, respectively [8].

Biochemical oxygen demand BOD_5; was measured by use of an Oxi-Direct Lovibond BOD meter. COD was measured by the potassium dichromate method. Orthophosphate ions (PO_4^{2-}) were measured colorimetrically, sulfate ions (SO_4^{2-}) by nephelometry, nitrate (NO_3^-) and nitrite (NO_2^-) ions by the salicylate method of Zamballi [8].

For the determination of acidity (percentage of oleic acid), 15 ml of olive oil mill wastewaters were transferred into three 50 ml beakers and dissolved in 10 mL of ethanol 97%. These fatty acids are titrated with NaOH solution (0.1 N) in the presence of phenolphthalein and continued up to pH8**.** A control test (without fat) was performed under the same conditions [2].

Table 2: **Average physicochemical parameters of each site**

	pH	Acidity	Cond	NO_2^-	NO_3^-	COD	BOD_5	TSS	Cl^-	PO_4^{2-}	SAL	SO_4^{2-}
S1	5,75	1,278	4,78	0,3275	0,1297	154	63,04	20	2,3	0,0153	6,2	2,816
S2	5,25	1,316	11,5	0,112	0,092	94	16,45	9,5	5,09	0,14	8,9	1,247
S3	5,69	1,284	8,51	1,39	1,8	71,6	41,82	5,36	0,284	0,029	6,7	1,327
S4	5,22	1,728	4,62	0,32	1,17	84,4	35,07	18,56	0,213	0,03	2,9	1,356

pH, Conductivity (mS/cm); TSS, total suspended solids (g/L); Cl^-, chloride (g/L); PO_4^{2-}, orthophosphate (g/L); SO_4^{2-}, sulfate (g/L); NO_2^-, nitrite (g/L); NO_3^-, nitrate (g/L); COD,Chemical oxygen demand (g O_2/L); BOD_5, Biochemical oxygen demand (g O_2/L); SAL,Salinity (mg/L) ; Acidity (mg/L).

RESULTS

Descriptive Statistics

Results of monitoring the physico-chemical parameters (table 3).

Table 3: Descriptive analysis of physicochemical parameters – measurements

Parameters	Minimum	Maximum	Mean	Standard deviation
pH	5,220	5,750	5,478	0,254
Acidity	1,278	1,728	1,402	0,197
Conductivity	4,620	11,500	7,353	2,983
NO_2^-	0,112	1,390	0,537	0,522
NO_3^-	0,092	1,800	0,798	0,755
COD	71,560	154,200	101,033	33,122
DBO_5	16,450	63,040	39,095	17,397
TSS	5,360	20,000	13,355	6,397
Cl^-	0,213	5,090	1,972	2,074
PO_4^{2-}	0,015	0,140	0,054	0,052
SAL	2,900	8,900	6,175	2,242
SO_4^{2-}	1,247	2,816	1,687	0,682

pH, Conductivity (mS/cm); TSS, total suspended solids (g/L); Cl^-, chloride (g/L); PO_4^{2-}, orthophosphate (g/L); SO_4^{2-}, sulfate (g/L); NO_2^-, nitrite (g/L); NO_3^-, nitrate (g/L); COD,Chemical oxygen demand (gO_2/L); BOD_5, Biochemical oxygen demand (g O_2/L); SAL,Salinity (mg/L) ; Acidity (mg/L).

Table 4 : Results of the oxidizable material and Ratios of COD, BOD_5, TSS

Study sites	M.O g/L	DCO/DBO_5	DBO_5/DCO	TSS/DBO_5
S1	**177,41**	**2,44 < 3**	**0,41**	**0,32**
S2	**64,23**	**5,71 > 3**	**0,18**	**0,58**
S3	**107,5**	**1,71 < 3**	**0,58**	**0,13**
S4	**98,27**	**2,41 < 3**	**0,42**	**0,53**

***O.M** : oxidizable material*

$$OM = \frac{2BOD5 + COD}{3}$$

Principal Component Analysis (PCA)

The first three principal axes are sufficient to describe the information provided by the data matrix. Indeed, the percentages of variance are 45,44% and 30,77% for the axes F1 and F2 respectively (figure 2). The total information is estimated to a percentage of 76, 22%. The principal component analysis (PCA) [9] was conducted to identify the link between the different variables.

Correlations between variables and factors:

	F1	F2	F3
pH	-0,602	0,726	-0,331
Acidity	0,602	-0,726	0,331
Cond	0,647	0,595	-0,476
NO_2^-	-0,729	-0,087	-0,679
NO_3^-	-0,459	-0,654	-0,601
DCO	-0,166	0,720	0,674
DBO_5	**-0,958**	0,225	-0,180
TSS	-0,521	0,219	0,825
Cl^-	0,418	**0,908**	0,024
PO_4^{2-}	**0,958**	-0,225	0,180
SAL	0,647	0,595	-0,476
SO_4^{2-}	**-0,917**	-0,029	0,398

DISCUSSION

The average pH of Oil Mill waste water (OMW) is acid in the range of 5,478 ± 0,254 marking the status of the batch of the pressure system of extraction for all four sites (Jdida Oued, El Mhaya , Road of Rabat and Sidi Bouzekri.

The average of conductivity is about 7,353 ± 2,983 (mS/cm) exceeding the national and international standards (limit values 1500 (uS/cm). These values remain below the ones of Sidi Kacem [10] that is about 23,35 ± 15,11 (mS/cm).
The salinity varies from 8,9 to 2,9 (mg/L) comparably to that of Sidi Kacem which is in the order of 13,99 (mg/L) [10].

COD is 101,033 ± 33,122 (g/L) this value is lower than that of [11] ; and the BOD_5 is averaging between 39,095 ± 17,397 (g/L). The average COD and BOD_5 obtained exceeds the norm wich is respectively of 25 (g/L) and 8 (g/L) are limit values of the wastewater of the olive oil extraction industries.

The average value of the nitrate and chloride are respectively of the order of 0,798 ± 0 ,755 (g/L) and 1,972 ± 2,074 (g/L). These values are lower than the results obtained by 12] and above the work [11]. The average value of the nitrate (NO_3^-) in the four sites exceeds the limit wastewater for irrigation which is 50 (mg /L).

Total suspended solids (TSS) is 13,35 + 6,397 (g/L) very high value comparably to that of [11,13, 14] .The stations **S1, S3 , S4** have a ratio of COD/BOD_5 less than 3 (Table 4) which explains the physicochemical treatment processes are more effective than biological [10] .

However for the station **S2** the ratio COD/BOD_5 is greater than 3 which could be explained by the organic matter that is not easily biodegradable because it is a system that requires press and a very thorough chemical treatment.

The results of this report provide an indication of the importance of the pollutant little or no biodegradable . [11] Similarly the ratio of BOD_5/COD = 0.18 of the station **S2** is lower than the results recorded by [10]. However, at levels the ration of BOD_5/COD lower than 0.30, the physico-chemical treatment processes are more efficient than those biological [10].

Cartesian diagram:

The Cartesian diagram (Figure 2) allowed us to identify four groups **G1, G2, G3** and **G4** .

G1: It covers pollution parameters such as COD, BOD_5 and TSS . These are highly correlated with station **S1**, which justifies that it is the most polluted of the four sites (Table 3).

G2: Encompasses the correlation between conductivity and nitrate was weakly significant , this could be explained by the mineralization of the effluent to the exit of the station is not necessarily due to sulphate ions , but can be other ions probably in water in particular , calcium ions , chlorides, etc. [7] .

G3 : The station **S3** indicates that it contains a lot of nitrate this could be explained by the quality of the water used in the three- phase system.

G4 : The station S4 is strongly correlated with the acidity , which is the most acidic pH of the four stations (Table 3) .

However changes in the parameters of the four sites studied is mainly due to the following factors **[15]**:

- Olives maturation Stadium,
- Climatic conditions,
- Variety of olive trees,
- Culture System,
- Location,
- Olives storage time before the crushing,
- Techniques and storage,
- Nature conservation olives,
- The process of olive oil extraction represents the single most importan.

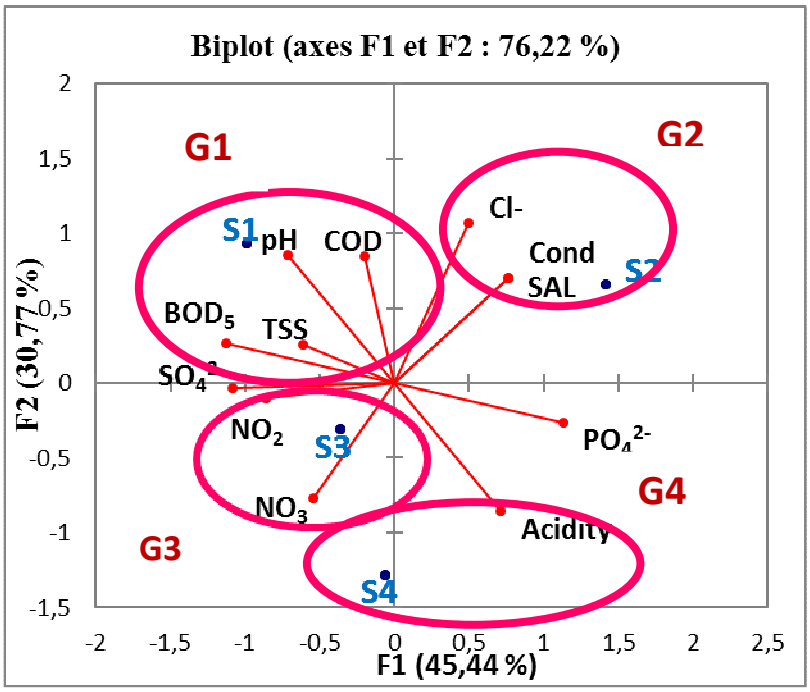

Figure 2: **Cartesian diagram showing the correlation between the physico-chimques parameters and stations**

CONCLUSION

The Oil Mill wastewater have a heavily polluted discharge residual liquid form of the composition of which is variable. This variability depends on the type of olives (the picholine Moroccan species is most dominant in Morocco) the degree of maturation

(according to collection period), cropping systems, salting practice for the conservation of olives, climatic conditions and the process used for the extraction of olive oil .

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