



Treatment of oil mill wastewaters by infiltration-percolation on two types of filters based on soil, sand and fly ash

E. El Herradi^{1,2*}, G. Boujaber¹, M. Naman³, A. Laamyem⁴,
C. El Adlouni⁵, F. Naman¹

¹Université Chouaïb Doukkali, Faculté des Sciences, Laboratoire de Biotechnologie Végétale, Ecologie et Valorisation des Ecosystèmes, El Jadida, Maroc

²Université Mohammed V, Ecole Normale Supérieure, Laboratoire de Physico-Chimie des Matériaux Inorganiques et Organiques (LPCMIO), Rabat, Maroc

³Institut Supérieur des Professions d'Infirmiers et Techniques de Santé (ISPITS), Laboratoire de Microbiologie, Casablanca, Maroc

⁴Université Chouaïb Doukkali, Faculté des Sciences, Laboratoire de la matière condensée, équipe de Physique de l'Environnement, Département de Physique, El Jadida, Maroc

⁵Université Chouaïb Doukkali, Faculté des Sciences, Laboratoire de Biotechnologies Marine et de l'Environnement, El Jadida, Maroc

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*Corresponding author. E-mail : haelherradi@yahoo.fr

Abstract

The olive oil extraction industry generates high amount of olive mill solid waste and olive mill wastewater. These effluents are heavily loaded with organic matter. Although they are rich in nutrients for plants, their discharges without any treatment affect the quality of water and soil and cause immense environmental damages. The objective of this study is the treatment of oil mill wastewaters of the city of Sefrou (Morocco) by infiltration-percolation on two types of filters. The first based on soil and sand (F1) and the second based on soil, sand and fly ash (F2). The results of the physicochemical analyses show that oil mill wastewaters have an acidic pH (4.48) and are a very high organic matter concentration (COD 329.68 g/L and BOD₅ of 20 g/L), suspended matter (5.7 g/L) and dissolved salts (13.18 mS/cm). The total polyphenol is 1.28 g/L. Their levels of trace metals are low except for iron where its content reached 78.17 mg/L. The treatment of oil mill wastewaters by both F1 and F2 filters has allowed an increase in the pH which becomes basic, a decrease in electrical conductivity, a significant removal of COD, BOD₅, total polyphenols, MES, nitrogenous materials, phosphate pollutants of elements analyzed and significant reductions of trace metals, respectively in F1 and F2. However, a release of the calcium element is observed at filter 2

Keywords : oil mill wastewaters, soil, sand, fly ash, infiltration percolation

1. Introduction

Morocco is one of the most olive-oil producing Mediterranean countries. Trituration of olives is done by a traditional sector constituted by craft units (maâsras) and a modern sector composed of semi-industrial and industrial units [1].

The olive oil extraction process produces, beside the noble "olive oil ", two by-products. One solid, grignons formed by olives pulps and cores and another liquid, oil mill wastewaters. These are constituted of olives vegetation water, washing water and added water during the oil extraction process.

As they are stocked, the oil mill wastewater's color gradually passes from brownish to dark with a turbid aspect and a more accentuated foul smell [2]. They are acids, have a strong saline load and are rich in organic matters and in polyphenols [3]. These characteristics confer on oil mill wastewaters a highly more marked pollution than urban wastewaters.

The quantity and composition of oil mill wastewaters depend on the olives variety, their maturation stage, the season of picking, climatic conditions, cultivation techniques, salting practices used for the olives conservation and on the olive oil extraction technology [4]. It is estimated that a kilogram of olives gives 1-1.5 liter of oil mill wastewaters [5]. In Morocco, the annual production of oil mill wastewaters is assessed at 250 000 m³ [6]. In most cases, they are poured out in their rough natural state into the environment or into the sewers causing serious pollution issues [3].

The objective of this work is to study the oil mill wastewaters treatment by infiltration-percolation, a technology reserved until now for the urban wastewaters treatments. Two types of filters are used in the hope of reusing treated oil mill wastewaters in agricultural irrigation. The filter 1 contains soil and sand (F1) and filter 2 contains soil, sand and fly-ashes (F2).

2. Materials and methods

2.1. Substrates used

The studied oil mill wastewaters were collected in a semi-industrial oil mill of Sefrou, a town located at the bottom of the middle Atlas at 850 m of altitude.

The filters used contain sand and/or soil and fly-ashes.

- The soil: is a cultivated soil of the EL Jadida region. The samples were taken at the level of the upper horizon 0-20 cm.
- The sand: is a sea sand of the Sidi Bouzid beach located at 5km in the south of EL Jadida, washed several times with clear water before its use.

The soil and sand samples were dried and sieved (2 mm)

- The fly-ashes come from the thermal power station JLEC of Jorf Lasfar, industrial park located 17 km south of EL Jadida. They are produced to the coal combustion and transported by smoke then collected the level of the electrostatic precipitators. These ashes are in the form of a soft fine pale grey power, similar to the cement.

2.2. Experimental device

The experimental pilot used consists of two columns in the form of funnel with 8 cm in diameter and 12 cm high. The columns are filled with a 10 cm thickness with 2 or 3 substrates. In the bottom of the column, a filter paper is placed to avoid the flow.

Filter 1 (F1): the column is filled with 3 layers, soil layer placed between two layers of sand.

Filter 2 (F2): the column is filled with 3 layers upwards, a layer of sand, a layer of fly-ashes and a soil layer.

The choice of this layout takes into account the granulometry of the materials to prevent their clogging. The two columns are prewashed several times with tap water before loading them by the oil mill wastewaters. The flow is done by percolation through the substrate.

2.3. Measured parameters

The different physicochemical parameters for used substrates, oil mill wastewaters and the percolats of the oil mill wastewaters treated (pH, electrical conductivity, suspended matter SM, COD, DBO₅, NH₄⁺, NO₃⁻, total phosphorus P_T, orthophosphates PO₄³⁻, chlorides, the granulometric analysis) were determined by standardized methods AFNOR [7]. Total nitrogen NTK is given according to the method of Kjeldahl described by Aubert [8]. The metal elements were analyzed by ICP (Inductively Coupled Plasma).

The total phenol content of olive oil mill wastewaters was determined with by spectrophotometry using the Folin-Ciocalteu method [9]. 0.5 mL portion of 10% Folin-Ciocalteu's reagent dissolved in water was mixed with 0.1 mL of the sample and allowed to stand for 3 min. Then, 1.5 mL of 2% of sodium carbonate was added to the mixture. After incubating 30 min in the dark, the absorbance was measured at 765 nm with UV-Visible spectrophotometer. Results were expressed as gallic acid equivalents.

The flow of infiltration was given using a chronometer and consists in calculating the quantity of water which crosses the filter during one minute.

3. Results and discussion

3.1. Characterization of the oil mill wastewaters

Table 1 shows the results of the physicochemical parameters of the studied oil mill wastewaters. It is deduced from this table that the oil mill wastewaters have an acid pH of 4.48. This value belongs to the interval 4.2-5.9 found by several authors [10, 11]. The acid feature of the oil mill wastewaters is due to their organic acids

wealth and the products of polymerization and self-oxidation reactions. These reactions are manifested by a change in the dark initial color of the oil mill wastewaters to a very dark black [12]. The conductivity of a value of 13.18 mS/cm, belongs to the field of conductivities (between 10 and 50 mS/cm) found by Tsioulpas and al. [13]. This value reflects the high percentage of salts present in these effluents due to the salting practices for the olives conservation before the trituration and the oil mill wastewaters natural resources in dissolved mineral salts. The studied oil mill wastewaters content of suspended matter (SM) is of 5.7 g/L. It exceeds the Moroccan norm of discharges. But this content remains lower than what was obtained by Ouabou and al. [14] which is of 10 g/L and exceeds by far what was obtained by Achak and al. and Hanafi and al. [15, 16, 17]. The content of SM decreases depending on the decanting process duration of the oil mill wastewaters.

Table 1- Physicochemical characteristics of oil mill wastewaters

pH	4.48
Electrical conductivity (mS/cm)	13.18
COD (g/L)	329.68
BOD ₅ (g/L)	20
Total polyphenols (g/L)	1.28
SM (g/L)	5.7
Total nitrogen (g/L)	0.68
Ammonium (mg/L)	1.04
Nitrates (mg/L)	5.94
Orthophosphates (g/L)	2.14
Total phosphorus (g/L)	0.82
Sulphates (g/L)	1.03
Chlorides (g/L)	1.055
Potassium (g/L)	1.002
Calcium (g/L)	0.316
Magnesium (g/L)	0.34
Sodium (g/L)	0.064
Iron (mg/L)	78.17
Zinc (mg/L)	5.09
Manganese (mg/L)	3.8
Aluminium (mg/L)	0.63
Copper (mg/L)	0.01
Chromium (mg/L)	0.018
Lead (mg/L)	0.025
Cadmium (mg/L)	0.0003

The biodegradable organic matter concentration (BOD₅) in oil mill wastewaters is 20 g O₂/L while the content of oxidizable organic matter (COD) is 329.68 g O₂/L. Even if oil mill wastewaters are rich in organic matters, their weak ratio BOD₅/COD (< 0.1) highlights a hardly biodegradable effluent. If the BOD₅ value of the oil mill wastewaters is lower than Esmail's and al. one [18], the COD value remains comparable with what was obtained by Ouabou and al. [14] and higher than what was found by the other authors [18, 19]. This is due to the strong degradation of the organic matter during the oil mill wastewaters stocking so that it makes them potential pollutants in case of discharge without any preliminary treatment.

The total polyphenol content of about 1.28 g/L. This value is in the range (0.24 to 11.75 g/L) reported by several authors in Bouknana et al. [10]. This concentration could possibly be the cause of the toxicity of vegetable with respect to biological activity.

The content of total nitrogen in oil mill wastewaters is 0.68 g/L. This one remains comparable to values obtained by several authors [20, 21]. The oil mill wastewaters concentration in ammonium (1.04 mg/L) is weak in comparison with those found by Achak and al. and Hanafi and al. [15, 17] which are respectively, in the order of 32 mg/L and 38.09 mg/L. Also, the oil mill wastewaters content of nitrates (5.94 mg/L) are weaker compared

with those recorded by Bouknana and al., and Ouabou and al., [10, 14]. The contents of total phosphorus and orthophosphates of the oil mill wastewaters are respectively 0.82 g/L and 2.14 g/L. These contents are superior to those reported by Achak and al. [16]. The oil mill wastewaters contents of these fertilising elements vary from an olive-growing company to another. They depend on the climatic conditions and the use or not of manures. The oil mill wastewaters thus constitute a source of nutritive elements which could replace chemical fertilizers.

The contents of potassium in oil mill wastewaters, magnesium, calcium and sodium are, respectively, 10 g / L, 0.34 g/L, 0.31 g/L and 0.064 g/L. These values remain rather low compared to those found in the literature [16]. The content of chloride ions in oil mill wastewaters is 1.05 g/L. This one is very close to that obtained by Mebirouk and al. [22] which is of 1.1 g/L. The content of sulphates in oil mill wastewaters is 1.03 g/L, a value which is within the range reported by Bouknana and al. (0.52 to 20.6 g/L) [10].

Contrary to the majority of the metal elements traces detected in the oil mill wastewaters, their iron content is higher (78.17 mg/L) and is more important than that found by Bouknana and al. [10] followed by those of zinc and manganese.

3.2. Characteristics of the soil, sand and fly ash used

The granulometric analysis of the two substrates soil and sand used in the two filters are indicated in table 2. This is a beach sand called coarse sand as the soil texture is sandy-loam with a high proportion of fine sand.

The soil has an alkaline pH and contains 1.35% organic matter. The sand has a strong alkaline pH that is due to the presence of carbonates and it is poor in organic matter.

Table 2 - Some physicochemical parameters of the soil and studied sand

	Soil	Sand
Granulometry (%)		
Coarse sand	25.6	96.5
Fine sand	49.6	0.6
Coarse silt	9.5	0.8
Fine silt	8.8	0.9
Clay	6.5	1.2
Chemical characteristics		
pH eau (1/5)	7.9	8.64
C.E (1/5) (mS/cm)	0.45	0.24
MO (%)	1.35	0.68
Total N (%)	0.087	0.02
N-NH ₄ ⁺ (mg/kg)	1.03	0.59
N-NO ₃ ⁻ (mg/kg)	5.6	0.26

Used fly ashes have a very fine texture because 97.3 % of their particles have a lower granulometry than 200 µm. The granularity of the grains lies between 5 and 20 microns. The refusal with the 80 micron sieve does not exceed 20 % in weight and that in the 50 microns sieve 40 %.

The ashes chemical composition is indicated in the table 3. They have an aluminosilicate texture since their percentage in oxides (SiO₂, Al₂O₃, and Fe₂O₃) is 94.4 %.

Table 3 - Chemical composition of the fly-ashes determined by ICP

Oxyde	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	MgO	SO ₃	P ₂ O ₅
% mass	57	34	3.4	10	1.2	0.12	0.02	0.5	1.1

The chemical characteristics of fly ashes samples are different from those reported by El Moudni El Alami et al. and Moufti et al. [23, 24]. This is probably due to the coal nature. In the case of fly ash used, this one is imported from several countries (America, the Southern Africa, Colombia, China and Russia). According to a study carried out by Pandey and Singh [25] conditions of combustion, the type of flue gas treatment and their storage mode. Fly ashes have an alkaline pH of 10.56 and an electric conductivity of 1.13 mS/cm.

The volumes of filtrates recovered after treatment are 99 and 93 mL for F1 and F2 respectively. The infiltration flow in filter 1 is 2.94 mL/min and 2.22 mL/min in filter 2. The residence time which is the time required for the passage of effluent in the column is 33 min 42 s and 41 min 56 s respectively in F1 and F2. This shows that the contact time is higher in the bracket with soil and ashes. The larger the particle size is small, the lower the residue of the effluent in the column is high which will influence the retention rate.

3.3. Purifying efficiency filters

3.3.1. Effect on pH

After purification of oil mill wastewaters by the filters F1 and F2, pH passes from 4.48 to 8.33 and 9.17 respectively. The increase in pH was also found by Achak et al. and Mekki et al. [15, 20]. According Zenjari and Nejmeddine [21] an increase in pH is attributed to the adsorption of organic acids responsible for the acid pH of oil mill wastewaters on the clay particles. It may also be related to neutralization of the oil mill wastewaters by the carbonates present in all levels. The pH values of the two filtrates are in the range of pH compatible with normal development of the microorganisms of the soil and the most crop plants and Moroccan norm of direct discharges [26].

3.3.2. Abatement of electrical conductivity

The electrical conductivity of oil mill wastewaters knows a sharp decrease after treatment with both filters. This passes of 13.18 mS/cm to 2.62 and 5.61 mS/cm, respectively F1 and F2. According to Sierra et al. [27] soil carbonates are responsible for the neutralization of the pH and decrease of the electric conductivity of the oil mill wastewaters. The amount of dissolved salts and thus ion after treatment decreased by 80.12% and 57.43%, respectively F1 and F2. The difference in reduction of the conductivity between the two filters is due to the presence of ash in F2 which have a higher EC (1.13 mS/cm). The conductivity values of the filtrates are lower than those found by Achak et al. [16]. According to these authors, the high electrical conductivity recorded is related to the leaching of sand minerals and mineralization of organic matter.

The filtrate F1 and F2 both have low salinity. Their concentrations in the soluble salts are considered limits (<12 mS / cm) [3]. These filtrates can be applied safely for irrigation of crops.

3.3.3. Abatement of suspended matter

The removal of suspended matter is considered as the essential process for the purification of waste water by the soil [27, 28, 29]. After the passage the oil mill wastewaters on filters F1 and F2, their contents of SM passes from 5700 mg/L to 150 and 45 mg/L, respectively, which represents an abatement of 97.36% for F1 and 99.21% for F2. The reduction by the two filters is mainly due to physical processes (filtration and sedimentation) and the compaction level of the filter substrate. The difference of abatement between the two filters is due to the presence of ash in the filter 2. These have a very fine particle size and thus a residence time of the higher effluent allowing a better retention of SM. The abatements levels found are similar to those cited by Achak et al. and Zenjari and Nejmeddine [15, 21].

3.3.4. Abatement of organic matter

The elimination of the organic matter of oil mill wastewaters is primarily through degradation, transformation and bacterial oxidation. Much of the organic material is removed by simple mechanical filtration through the filter bed. However, the oxidation of dissolved organic material is limited both by the availability of oxygen and by the residence time of the effluent at the gravel [30].

The organic matter content in oil mill wastewaters greatly decreases after passing through both filters. Indeed, COD passes from 329.68 g/L at 0.25 to 0.06 g/L in F1 and F2, respectively, which corresponds to a reduction rate of over 99.92%. Such rate was also obtained by Achak et al. and Zenjari and Nejmeddine [16, 21]. While BOD₅ passes from 20 g/L to 0.1 g/L and 0.02 g/L, respectively, in F1 and F2 corresponding to the reduction rate of 99.5% and 99.9%. The sharp reduction of the organic matter content is the result of improved mineralization or oxidation of organic matter. This abatement of the organic matter indicates that a good bacterial assimilation took place in both filters. This is probably due to better oxygenation of aerobic bacteria present in both filters.

3.3.5. Abatement of different forms of nitrogen

The nitrogen removal by a processing system depends on its chemical form (organic nitrogen, nitrate and ammonium). The residual organic nitrogen associated with SM is removed either by attachment in the first

centimeters of the soil (sedimentation and filtration) or by the uptake by microorganisms or mineralization. Ammonium nitrogen (NH_4^+) is removed by volatilization as NH_3 or biological oxidation leading to the formation of nitrites immediately converted into nitrates by nitrifying bacteria [2].

After the passage of oil mill wastewaters on both filters, the total nitrogen content passes from 686 mg/L to 9.8 and 12.55 mg/L for F1 and F2, respectively. This corresponds to a reduction rate of more than 98% for both filters. Such rates are close to the one found by Zenjari and Nejmeddine which is about 96% [21]. Unlike F1, where a slight decrease of the content of NH_4^+ and NO_3^- in oil mill wastewaters was observed with the F2. There has been a sharp increase in the form of nitrate nitrogen moving from 5.94 mg/L to 30.69 mg/L.

According to Ouazzani [31], the ventilation filter conditions used were behind the strong adsorption of ammonium ions on the particles of sand and organic particles before nitrification. Although F2 filtrate nitrate levels are increasing, they remain close to the threshold limit values tolerated in irrigation by treated wastewater (30 mg/L) [26, 32].

3.3.6. Abatement of other chemical elements

The result of the reduction of the chemical elements of the oil mill wastewaters by the filters F1 and F2 is shown in Figure 1. For both filters, the abatement of PO_4^{3-} and P_T is about 99%. With these two filters, the impact of phosphate pollution on the receiving sites is limited. These rates are similar to those found by Zenjari and Nejmeddine [21]. These authors found a reduction for PO_4^{3-} and the P_T of 99.5% and 98.8% respectively on a sandy-loam soil filter.

Calcium was present in the oil mill wastewaters with an initial concentration of 316 mg/L. The evolution of this concentration in F1 percolate level marked a fall with a decrease of 72.61%. For cons, the evolution of calcium in the F2 percolate recorded an increase with a rate of over 84% compared to the raw OMW. This may be due to the wealth of fly ash of CaO. The potassium recorded a reduction of 89.19% in F1 and 90.47% in F2. The magnesium and chloride have experienced reductions of 80.56% and 47.48% respectively in F1. Whereas they recorded only 45.27% and 22.72% from abatement in F2. Although the content of sodium in OMW recorded an increase with two filters, those remain within the limit of 500 mg/L proposed by [32]. Indeed sodium retention by the soil is not complete; salting can occur causing this element in drainage water [28].

3.3.7. Abatement of trace metals

The result of the reduction of trace metals of the OMW by the filter F1 and F2 is reported in Figure 2. The purifying performance of trace metals by the two filters are almost 100% except that the aluminum and the chrome which remain below the standards established for irrigation water which is 5 mg/L for aluminum and 1 mg/L for chromium [26, 32]. The abatement rate of aluminum is 65.4% for F1 and F2 to 72.5%. For chromium, abatement rate is 27.78% for F1. For F2, the chromium content increase is 7.5% and reaches a value 0.24 mg/L. This is due to the wealth of fly ash in this element (142 mg/kg).

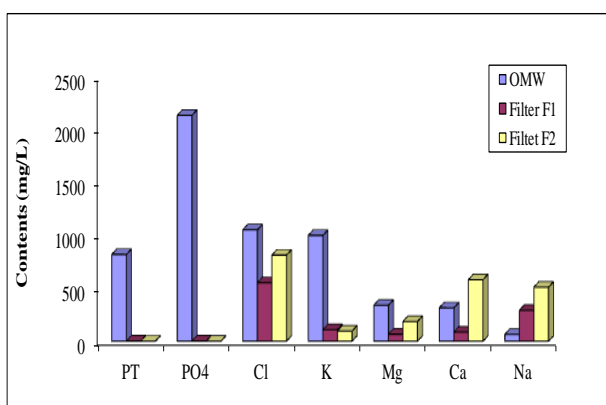


Figure 1 - Abatement of major elements by the two filters

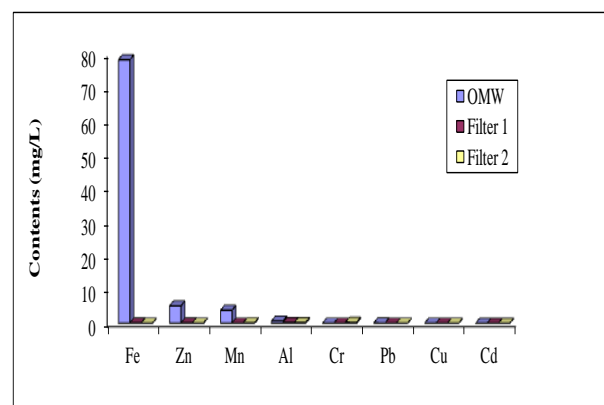


Figure 2 - Abatement of trace metals by the two filters

It is interesting to note that despite the high content of iron in vegetable water, both filters enabled its total abatement. The physicochemical parameters of the substrates affect the concentration of the metallic elements

and decide to transfer to a carrier or another [33]. Indeed, the pH to weakly alkaline medium limits the mobility of metal and promotes their retention by the particles of substrate [34]. According Bigorre [35], the organic material has a high capacity to bind heavy metals. This ability varies depending on the concentration and nature of the ion and pH.

3.3.8. Abatement of total polyphenols and coloring

The initial concentration of polyphenols in oil mill wastewaters was 1.28 g/L. After treatment, it becomes 0.083 and 0.075 g/L for F1 and F2. This indicates that the removal efficiency of polyphenols is about 93.52 % and 94.14 %, respectively.

Figure 3 shows the degree of discoloration of the raw OMW from reddish-brown to black in color after their treatment by the two filters. F2 has a bleaching power higher than F1. This is explained by the wealth of silica fly ash, alumina and iron oxide that secure organic and inorganic load of the effluent. The latter has a strong complexing power of colloidal materials [24]. According Bambalov et al. [36], the color variation raw OMW is due to several factors including the variety and ripeness of the olives, the freshness of the OMW, the proportion of phenolic compounds and their state of degradation [36]. For Dhoubi et al. [37], the coloration of treated vegetable water abatement can be explained by the polymerization and / or bioconversion of their compounds and by changing their pH. According to Dommergues [38], the degradation of phenolic compounds by the bacteria may be accelerated by an increase in pH and / or improved ventilation. Indeed increasing the pH of the vegetable after their application on the ground leads to the transformation of phenols phenates training $C_6H_5O^-$ ions [39]. These latter are secured by the cations of aluminum and iron oxides, the calcium carbonates and silicates of the substrates used.

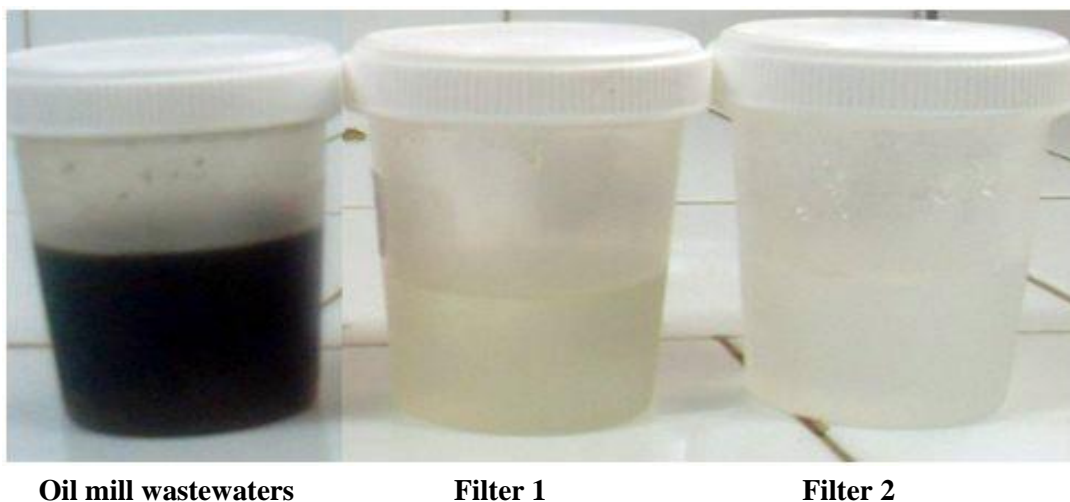


Figure 3 -Photograph showing the discoloration of the OMW by the two filters

Conclusion

Analysis of oil mill wastewaters used shows that they have a very acidic pH and is very loaded with organic matter, suspended solids and dissolved salts (potassium, chloride, magnesium). The iron element is the most abundant heavy metal among the existing ones.

After treatment of oil mill wastewaters by the two filters F1 (sand-soil-sand) and F2 (fly-ground sand-ash), the pH becomes slightly alkaline, there is also reduced electrical conductivity, a significant COD removal of BOD₅, SM, nitrogenous matter, phosphate pollutants and significant reductions of dissolved salts. The F2 gave better abatement for many of these elements than F1 which can be justified by a longer contact between the effluent and filter substrates.

After treatment of oil mill wastewaters filters F1 and F2 by the rate of reduction of iron, zinc and manganese exceeds 99% for both filters. For aluminum, the abatement rate is over 65%. Although the content of chromium in the treated vegetable water F2 is greater than that contained in the raw vegetable water, it remains below the limit value set by the irrigation standards. Compared to the raw vegetable water, those treated with the two filters undergo a severe discoloration and in particular to the filter 2.

Of all the results obtained, the high abatement rates obtained in almost all the physicochemical parameters measured of oil mill wastewaters processed by the two filters show the interest of infiltration as of vegetable processing technique. Before using these oil mill wastewaters processed in the field of irrigation, extensive further study of their microbiological load and their agronomic value are essential.

References

1. MAPM, Ministère de l'Agriculture et de la Pêche Maritime (2013).
2. Mouncef M., Tamoh S., Faid M., Achkari Begdouri A., *Grasas y Aceites*, 44 (6) (1993) 335.
3. Ranalli A., *Olivae*, 37 (1991) 30.
4. Mert B. K., Yonar T., Kilic M., Kestioglu K., *J. Hazard. Mater.* 174 (2010) 122.
5. Leger C.L., *OCL-OL CORPS GRAS LI*, 6 (1999) 60.
6. MAEE, Ministère de l'Aménagement du territoire, de l'Eau et de l'Environnement, Secrétariat d'État chargé de l'Environnement, Rabat, Maroc, (2005).
7. AFNOR, Recueil de normes françaises : eau, méthodes d'essai, 2^{ème} Édition, Paris, France, (1983) 621p.
8. Aubert G., Méthodes d'analyse des sols. Éditions C.R.D.P., Marseille, France, (1978) 360p.
9. Singleton V. L., Orthofer R., Lamuela-Raventós R. M., *Method Enzymol.* 299 (1999) 152.
10. Bouknana D., Hammouti B., Salghi R., Jodeh S., Zarrouk A., Warad I., Aouniti A., Sbaa M., *J. Mater. Environ. Sci.* 5 (4) (2014) 1039.
11. Eroglu E., Eroglu I., Gündüz U., Yücel M., *Bioresource Technol.* 99 (2008) 6799.
12. Hamdi M., *Environ. Technol.* 14 (1993) 495.
13. Tsioulpas A., Dimou D., Iconomou D., Aggelis G., *Bioresource Technol.* 84 (2002) 251.
14. Ouabou E., Anouar A., Hilali S., *J. Appl. Biosci.* 75 (2014) 6232.
15. Achak A., Ouazzani N., Mandi L., *Rev. Sci. Eau*, 22 (2009) 421.
16. Achak A., Ouazzani N., Mandi L., *Rev. Sci. Eau*, 24 (2011) 35.
17. Hanafi F., Sadif N., Assobhei O., Mountadar M., *J. Water Science*, 22 (4) (2009) 473.
18. Esmail A., Abed H., Firdaus M., Chahboun N., Mennane Z., Berny E., Ouhssine M., *J. Mater. Environ. Sci.* 5 (1) (2014) 121.
19. Fakharedine N., Ouadghiri M., Amar M., Winterton P., Hafidi M., Ouhdouch Y., *Eurasia J. Biosci.* 5 (2011) 127.
20. Mekki A., Dhouib A., Sayadi S., *J. Environ. Manage.* 84 (2007) 134.
21. Zenjari B., Nejmeddine A., *Agronomie*, 21 (2001) 749.
22. Mebirouk M., Sbai L., Lopez M., Gonzalez J., *Grasas y Aceites*, 58 (2007) 366.
23. El Moudni El Alami S., Monkade M., Lahlou K., *Déchets*, 56 (4) (2009).
24. Moufti A., Mountadar M., *Water Qual. Res. J. Canada*, 39 (2) (2004) 113.
25. Pandey, V.C., Singh N., *Agric. Ecosyst. Environ.* 136 (2010) 16.
26. SEEE, Secrétariat d'État chargé de l'Eau et de l'Environnement, Normes de qualité : eaux destinées à l'irrigation (2007).
27. Sierra J., Marti E., Montserrat G., Cruanas R., Garau M.A., *Sci. Total Environ.* 279 (2001) 207.
28. Landreau A., *B.R.G.M.* (1987) 1.
29. Legeas C., *Sciences et Techniques de l'Eau*, 27 (2) (1994) 19.
30. Brissaud F., Lefevre F., Joseph C., Alamy Z., Landreau A., *IAHS Publ.* 188 (1989) 443.
31. Ouazzani N., Thèse de Doctorat, Marrakech, Maroc, (1998) 221p.
32. USAID, United States Agency for International Development, (2013) 58p.
33. Greffard J., Sarcia G., Bourg A., *Hydrologie*, 1 (1985) 55.
34. De Wit C.T., *Agric. Sys.* 40 (1992) 125.
35. Bigorre F., Thèse de doctorat. Université Henri Poincaré-Nancy, France, (2000).
36. Bambalov G., Israilides C., Tanchev S., *Biol. Wastes*, 27(1989) 71.
37. Dhoubi A., Aloui F., Hamad N., Sayadi S., *Proc. Biochem.* 41 (2006) 159.
38. Dommergues Y., *la vie dans les sols, aspects nouveaux, études expérimentales*, Eds Gauthier-Villars, Paris, France, (1971) 423.
39. Macheix J. J., Flauriet A., Billot J., Fruit phenolics, CRC Press Inc, ISBN 9780849349683, 392p.