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ORIGINAL PAPER

Olive mill wastewater disposal in evaporation ponds in Sfax (Tunisia): moisture content effect on microbiological and physical chemical parameters

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Abstract The study of the isotherms desorption of olive mill wastewater (OMW) was investigated to describe its water activity under different saturated environments. The microbial biodegradation of OMW during its storage in 5 evaporation ponds located in Agareb (Sfax-Tunisia) was carried out during the oil-harvesting year held 105 days in 2004. Gravimetric static method using saturated salt solutions was used and OMW as placed at 30°C and under different water activities ranging from 0.11 to 0.90. Eight models were taken from the literature to describe experimental desorption isotherms. During storage, the evolution of physico-chemical parameters including pH, temperature, evaporation, humidity, total phosphorus, chemical oxygen demand (COD), biological oxygen demand (BOD) and phenols and three microbiological flora (aerobic mesophilic bacteria, yeasts and moulds) were considered. At 30°C, when relative humidity increased in the experimented ponds of 69, 84 and 90%, the evaporation speed decreased from 1.24×10^{-5} to 5×10^{-6} cm^3 s^{-1}, from 6×10^{-5} to 7×10^{-6} cm^3 s^{-1} and from 5×10^{-6} to 1.1×10^{-7} cm^3 s^{-1} respectively. The desorption isotherm exhibited a sigmoidal curve corresponding to type II, typical of many organic material. The GAB and Peleg models gave the best fit for describing the relationship between the equilibrium moisture content and water activity in OMW ($R^2 = 0.998$). During the storage period, the analysis showed an increase of all the physico-chemical parameters studied, except phenols and total phosphorus concentrations. The microbiological study showed the predominance of yeasts and moulds and the decrease of bacteria population after 75 days reflecting both effect of recalcitrant compounds and the water activity on microbial growth.

Keywords Evaporation ponds · Isotherms · Water activity · Olive mill wastewater

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Introduction

In the Mediterranean countries, olive oil production represents ca. 98% of the total worldwide production (Paredes et al. 1999), and the disposal of olive oil mill wastewater (OMW) rise a major social, economical, and environmental problem in these Mediterranean olive oil producing countries (Plaza et al. 2007; Jarboui et al. 2008). The amplitude of the environmental impact of the 10 million m^3 of OMW produced yearly generated from three-phase systems represents the equivalent of wastewaters generated by 20 million inhabitants (McNamara et al. 2008). Indeed, OMW contains a high organic load including carbohydrates, nitrogenated compounds, organic acids, polyalcohols, a residual oil emulsion (Garcia-Gomez et al. 2003) and a high content of phytotoxic and antibacterial phenolic substances, which are recalcitrant to the biological degradation (Aktas et al. 2001). Moreover, OMW is characterized by a high potassium concentration and notable rates of nitrogen, phosphorus, calcium, magnesium and iron, which can play an important role on soil fertility (Angelidaki and Ahring 1997; Hachicha et al. 2006, 2008; Jarboui et al. 2008; Sellami et al. 2008). Such high organic load has a toxic effect, especially on fungal spore germination and methanogenic bacteria (Mechri et al. 2008). Furthermore, the high polyphenol and fatty acid contents of these wastewaters can inhibit the growth of microorganisms and hinter conventional secondary and anaerobic treatments in municipal treatment plants (Tsioulpas et al. 2002; Casa et al. 2003; Ben Sassi et al. 2006).

Several studies dealing with OMW chemical characterization are available, but published results are very variable because of the variability of some factors, such as climatic conditions, olive cultivars, degree of fruit maturation, olive storage duration and conditions, and oil extraction procedure (Aktas et al. 2001; Ben Sassi et al. 2006; Casa et al. 2003; D'Annibale et al. 2006; Fiorentino et al. 2002; Mouncif et al. 1995; Robles et al. 2000; Vitolo et al. 1999). On the other hand, little is known about the microbial flora of OMW.

In some olive oil producing countries, the OMW is often collected in open-air lagoons, then used as soil amendment without any further treatment (Jarboui et al. 2008; Sierra et al. 2001). This long storage period can be considered as a natural biological treatment method, where high evaporation conditions prevail during summer period in the Mediterranean countries. However, in spite of OMW water activity and environmental relative humidity affecting the evaporation process, the microbial community active in the ponds, and heterogenous aerobic and anaerobic flora, including both bacteria and fungi, characterize the storage-pond environment (Sellami et al. 2007; Jarboui et al. 2008; Hachicha et al. 2009).

The aim of the present work was to study the effect of moisture and water activity on evaporation process affecting the biological activity, and the evolution of microbiological and some physico-chemical parameters, describing the OMW composition progress during its storage in evaporation ponds.

Materials and methods

Study site and operation conditions

The study was conducted from March to July 2004, in 5 evaporation ponds. The OMW samples were collected from the evaporation ponds in the region of Agareb, located at 20 km in the South of Sfax, an important industrialized city in Tunisia (34°43′ North–10°41′ East; Fig. 1). The plant is made up of huge evaporation ponds, covering more than 57 ha (storage capacity of 523,335 m^3) and including 16 ponds and 7 newly extended ones. All of them are uncovered and connected by underground channels. They usually contain OMW during most of the year, except for the short spring period, when the concentrated fatty layer is collected for soap manufacturing, and the remaining OMW is drained into drying ponds. The connection allows the drainage of the OMW from one pond to another. These ponds have different dimensions (height, width, length) and hence various storage capacities. During the study, the OMW stored volume varied in each pond according to the effluent volume discharged. In the course of the experiment, the climatic conditions were those of Sfax city, with the monthly rainfall of 2–70 mm day^{-1}, humidity of 40–80 mm day^{-1} and temperature of 12–30°C. The evaporation varied between 30 and 230 mm and the wind blew between 1.5 and 23 m s^{-1} (INM 2004).

OMW samples

Samples were collected from 5 evaporation ponds: B1 (reception pond), B4, B5, B6 and B7, and sampling was made periodically each 15 days, starting from March until July 2004. Sample consisted of homogenizing a mixture of six sub-samples taken at

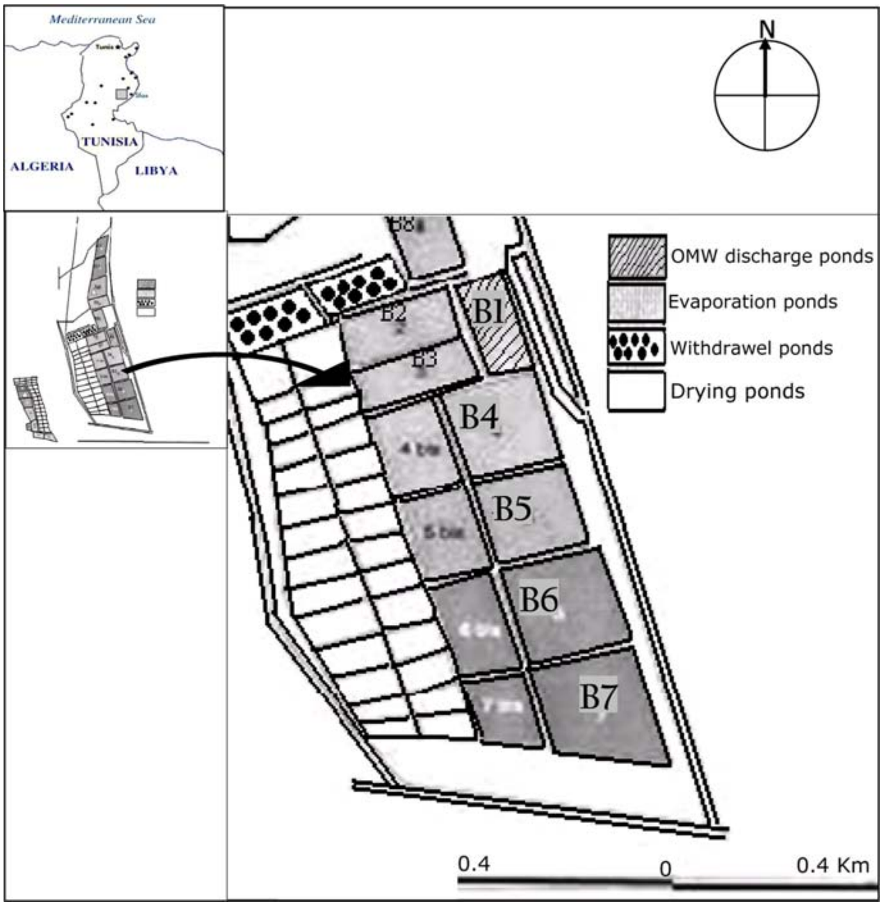

Fig. 1 Schematic plan of the OMW evaporation ponds in Sfax (Tunisia), showing 16 storage ponds, 7 extended part with 28 drying ponds (Total storage capacity: 523 m^3)

six different locations spanning the whole perimeter pond. Two sub-samples were collected at the middle of each pond-width, and two other sub-samples, each one at the third of the pond-length were equally sampled. All the ponds have the same heigt: 1.75 m. The length and the width of the sampled ponds are as follows: B1: 107.00 × 66.80 m, B4: 94.35 × 92.40 m, B5: 91.15 × 90.75 m, B6: 104.00 × 103.40 m and B7: 114.40 × 109.00 m. Water sampling bottle with sample container was used for sampling according to Japanese standards (JIS 1995; Ammar and Ueno 1999). This was first centrifuged at 1,610 *g* for 15 min (Sigma Laboratory centrifuges 4K15, rotor: 12,169-H), and the supernatant layer was physico-chemically and microbiologically characterized. This investigation was performed starting from the olive harvesting (March 2004) and remained almost 5 months (till July 2004). This period exceeded 1 month after the period of OMW discharge in the ponds.

Analytical methods

Desorption isotherms

The desorption isotherms of OMW were determined using the standard static gravimetric method of saturated salt solutions (Dumoulin et al. 2004) at 30.0 ± 0.1°C. The apparatus used consisted of sorption container equipped with a weighing dish in which the sample was exposed to humid atmosphere. Experiments were performed in a relative humidity range varying from 11 to 90%. Each salt solution provided a fixed relative humidity at 30°C. Seven saturated salt solutions were used. These were LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $SrCl_2$, KCl and $BaCl_2$ (Table 1). As indicated in Table 1, the saturated salt solutions used allowed to experiment water activity ranging from 0.111 to 0.898 (Dumoulin et al. 2004). Each salt solution was prepared by dissolving appropriate quantities of salt in distilled water to form

Table 1 The water activity (a_w) and relative humidity (RH) of saturated salt solutions at 30°C (Dumoulin et al. 2004)

Salt	LiCl	$MgCl_2$	K_2CO_3	$Mg(NO_3)_2$	$SrCl_2$	KCl	$BaCl_2$
a_w	0.1116	0.3238	0.4317	0.5133	0.6911	0.8362	0.8980
RH (%)	11	32	43	51	69	84	90

saturated solutions, and placed in a glass jar (Motarjemi 1988). A dish support was placed inside each jar with OMW sample. The jar was then held in the controlled container for 24 hours to stabilize at 30°C. Inside the jar, the sample was exposed to humid atmosphere. The relative humidity (RH) provided the defined water activity (a_w), according to the studied temperature. Samples were weighed at regular intervals and the equilibrium was judged to have been riched when the difference between the three successive weighing did not exceed 1 mg. The OMW dry matter content was determined at 105 ± 1°C for 24 h (AOAC 1996). The OMW equilibrium moisture content: X_{eq} was determined as follows (1):

$$X_{eq} = \frac{m_w - m_d}{m_d} \qquad (1)$$

where m_w is the mass before drying (g) and m_d the mass after drying (g).

The equilibrium moisture content (EMC) was obtained by dehydration of the OMW sample in a drying oven equipped with a Mettler-AT 400 ($\pm 10^{-4}$ g) analytical balance, connected to a personnel computer for data acquisition (sample weighing and time). The experiment ended when the sample moisture content reached an equilibrium state where the water activity (a_w) of the OMW could be expressed as a function of the RH of the atmosphere in the jar (a_w = RH/100). This moisture value was measured (weight variation less than 0.001 after 24–48 h, depending on the salt used; Hadrich et al. 2008).

The experimental desorption isotherms data were fitted using several mathematical models chosen among relevant isotherm equations most widely used to describe the sorption behavior of organic material products (Table 2; Jayendra Kumar et al. 2005; Hadrich et al. 2008; Sinija and Mishra 2008). The isotherm models used were those based on an absorbed monolayer of water (BET model), a multilayer and condensed film (GAB model), semi-empirical (Halsey model) and purely empirical models (Oswin, Smith, Handerson and Mizrahi models). A non linear regression analysis performed by Curve-Expert (version 1.37) software was used to fit the experimental desorption isotherms data. Two statistical parameters were used to determine the quality of

Table 2 Models used for fitting the experimental desorption isotherms of OMW and estimated parameters for the selected models of desorption isotherm equations for OMW at 30°C

Model	Parameters				Correlation coefficient (*R*)	Standard erreur (*S*)
	a	b	c	d		
GAB*: $X_{eq} = abca_w/((1-ba_w)(1-ba_w + aba_w))$	2.5627	0.9173	0.1571	–	0.9985	0.0187
Peleg**: $X_{eq} = aa_w^b + ca_w^d$	0.3311	0.8839	1.0209	6.2754	0.9989	0.0186
Oswin*: $X_{eq} = a(a_w/(1-a_w))^b$	0.2027	0.6491	–	–	0.9975	0.0221
Handerson*: $X_{eq} = (-\ln(1-a_w)/a)^{(1/b)}$	2.7187	0.8379	–	–	0.9971	0.0237
Modified Mizrahi***: $X_{eq} = (a + a_w(ba_w + c))/(a_w-1)$	0.0060	0.3026	−0.3730	–	0.9958	0.0325
Modified Halsey**: $X_{eq} = (-a/\ln(a_w))^{(1/b)}$	0.0859	1.3000	–	–	0.9938	0.0352
Smith**: $X_{eq} = a + b\log(1-a_w)$	−0.0321	−0.3592	–	–	0.9926	0.0384
BET*: $X_{eq} = aba_w/((1-a_w)(1-a_w + ba_w))$	0.0896	27.8336	–	–	0.9868	0.0509

a, b, c, and d: the constants of the different models; X_{eq}: the equilibrium moisture content (kg kg^{-1} d.b.); a_w: the water activity

* Hadrich et al. (2008)

** Sinija and Mishra (2008)

*** Jayendra Kumar et al. (2005)

the fit: the standard error (*S*) and the correlation coefficient (*R*) (Hadrich et al. 2008).

Physico-chemical analyses

The evaporation rate and the RH were calculated from the meteorological monthly tables of the National Institute of Meteorology (Institut National de Météorologie INM 2004). Physico-chemical characterization was made according to French standards methods (AFNOR 1997). The ambient temperature and the OMW sampled temperature were measured using a thermometer. The pH was directly measured in the sample with a Metler MP 225 metter. The chemical oxygen demand (COD) was determined using the method described by Knechtel (1987), using relatively small volumes of reagents and sample, respectively 2.8 ml of acidic hydrolyzing solution with 1.2 ml of oxidizing solution and 2.0 ml of the sample. The oxidation reaction was held at 150°C for 2 h. The biological oxygen demand (BOD) was measured by the manometric method with a respirometer BSB-Controller, Model 620 T.WTW. Polyphenols (Pphe) and phenol (Phe) contents were respectively measured by gravimetric method after extraction and Folin-Ciocalteau reagent (Merck), using catechol as standard (Box 1983; Chtourou et al. 2004). Total phosphorus was determined colorometrically as a molybdovanadate phosphoric acid complexe.

All parameters were analyzed in triplicate

Microbial enumeration

For microbial enumeration, the OMW (10 ml) was suspended in sterile physiological water (90 ml). The suspension was used for microbial counts by cell enumeration expressed as total number of colony forming units (CFU) according to ISO 7218 (1985). Serial decimal dilutions of each suspension were plated in triplicate on different agar media: Plate Count Agar (Pronadisa, Madrid-Spain), for the total aerobic mesophilic bacteria incubated at 37°C for 24 h, and oxytetracyclin glucose agar (Pronadisa, Madrid-Spain) for yeasts and moulds enumeration, incubated at 25°C for 5 days (AFNOR 1995). The microbial results were expressed by calculating the ratios of decimal logarithmic value of each flora (bacteria, moulds and yeasts).

Statistical analysis

Physico-chemical and microbial parameters are presented as average values of three replicates. Basic statistical analysis of the data was performed using ANOVA software for windows. Statistical significance was defined for $P < 0.05$.

Results and discussion

OMW isotherms desorption

The influence of water activity on spoilage is an important factor. Moisture content and water activity affect the progress of chemical and microbiological spoilage reaction. The organic material (OM) corresponds to the lower part of the sorption isotherm. This includes water in the monolayer and multilayer category.

The experimental results of the OMW desorption isotherm with the specific moisture content at 30°C and at different RH are presented in Fig. 2. Moisture content decreases with drying time to reach an equilibrium moisture value (Fig. 2a). The experimental results may explain the evaporation speed in evaporation ponds at different RH. The evaporation speed varied from 5×10^{-5} to 5.8×10^{-6} cm^3 s^{-1}, from 4×10^{-5} to 5×10^{-6} cm^3 s^{-1}, from 3×10^{-5} to 3.6×10^{-6} cm^3 s^{-1} and from 2×10^{-5} to 3×10^{-6} cm^3 s^{-1} in RH 11, 32, 43, and 51% respectively. When RH increased, the evaporation speed decreased from 1.24×10^{-5} to 5×10^{-6} cm^3 s^{-1}, from 6×10^{-5} to 7×10^{-6} cm^3 s^{-1} and from 5×10^{-6} to 1.1×10^{-7} cm^3 s^{-1} for 69, 84 and 90%.

The desorption isotherm exhibited a sigmoidal curve typical of the most organic material products and corresponding to type II curves according to the classification of Brunauer et al. (1938). The EMC increased with RH and may predict the effect of the RH on OMW storage and their evaporation especially in summer period when temperature increased (Fig. 2b).

Three regions may often be identified. In region A ($a_w < 0.2$), the water is strongly absorbed to the OM as a monolayer. The water in region B ($0.2 < a_w$

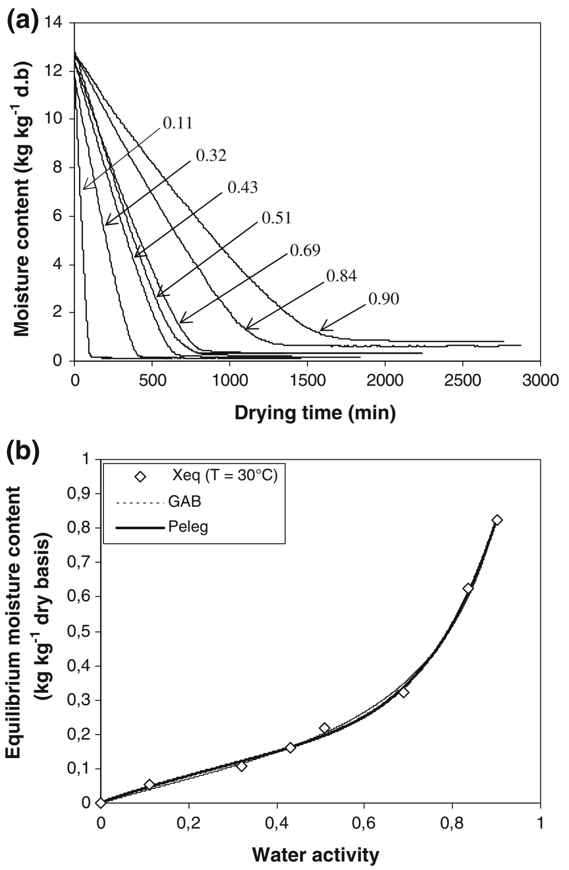

Fig. 2 OMW isotherm desorption study: X_{eq}: the equilibrium moisture content at constant pressure and temperature

< 0.7) is less strongly held in additional hydrogen bonded layers and in small capillaries. In region C ($0.7 < a_w < 1.0$), the water is condensed in larger capillaries or other larger spaces or is free in solution (Christian 2000).

The EMC plays a particularly important role at the end of drying. The quality of most organic material preserved by drying, depends on a great extent upon their physical, chemical and microbiological stability. This stability is mainly a consequence of the relationship between the EMC of the organic material (Sinija and Mishra 2008). The results of non linear regression analysis of desorption isotherms obtained for the tested models are presented in Table 2. It can be observed that all models have high correlation coefficients ($R > 0.98$) and significant standard errors ($S \leq 0.05$). The GAB and Peleg models were the most suitable for describing the relationship between the EMC and water activity in tested OMW. A comparison between experimental and calculated GAB and Peleg models values of desorption isotherms of OMW obtained at 30°C is presented in Fig. 2b. Both models follow the same trend with the same correlation coefficient ($R = 0.998$) and standard error ($S = 0.0186$). The GAB equation is a multilayer model that takes into account different properties of water in the multilayer region. It fits the sorption isotherm data of a variety of food products, with a good correlation of the 75% of the food isotherms studied. Peleg developed a polynomial equation to calculate the moisture content for the material as a function of the water activity (Heldman and Lund 2007). Some authors used the same models to fit the isotherms of some food products (Goula et al. 2008; Jayendra Kumar et al. 2005; Sinija and Mishra 2008; De Temmerman et al. 2008).

During OMW storage in open ponds, physico-chemical transformations occur depending on water availability and mobility in the effluent. Indeed, water can be bounded to polar groups, it may establish hydrogen bound, and acts as solvent or as reagent in hydrolysis reactions. The desorption isotherm informs about the water in a product at atmospheric equilibrium state allowing the product transformations during storage. The water activity characterizes biological reactions and at relatively high levels it enhances microbial enzymatic activities, leading to degradation of organic compounds easily metabolized. Bacterial growth is inhibited below water activity of 0.9 and moulds and yeasts are usually inhibited below 0.70 and 0.80 respectively. Although some osmophilic yeasts strains grow at water activities lower than 0.6, most enzymes are inactive when the water activity is below 0.85. Such enzymes include amylases, phenoloxidases and peroxidases. However, lipases may remain active at value as low as 0.3 (De Man 1999). The reaction rates in organic material products as determined by water activities are presented in Table 3.

Effluent parameters evolution in the studied ponds

Temperature, evaporation and RH

The temperature, calculated evaporation and RH evolutions are presented in Fig. 3. The ambient temperature progress was globally comparable to

Table 3 Reaction rates in organic materials products as determined by water activity (De Man. 1999)

Reaction	Monolayer water	Capillary water	Water activity
Enzyme activity	Zero	Low	0.3–0.8
Microbial growth			
Molds	Zero	Low	0.70–0.85
Yeasts	Zero	Low	0.80–0.90
Bacterial	Zero	Zero	0.90–0.98
Hydrolysis	Zero	Rapid increases	0.0–0.25
Non enzymatic browning	Zero	Rapid increases	0.0–0.25
Lipid oxidation	High	Rapid increases	0.3–0.8

Loosely bounded water is high

that of evaporation ponds. It increased with time reflecting hot season occurrence and fluctuated between 25 and 35°C. However, a specific temperature decrease was noticed on day 45, related to meteorological conditions, when a rainfall equal to 12 mm was registered, the highest relative humidity value was 60% and the lowest evaporation rate and wind speed intensity were 42 mm $days^{-1}$ and 1.75 m s^{-1} respectively (Institut National de Météorologie INM 2004). The calculated RH and evaporation rates varied from 40 to 70% and 25 to 100 mm $days^{-1}$ respectively. According to these values, the evaporation effect seems to be tightly dependent on seasonal variations.

The comparison of temperature evolution in the 5 studied ponds showed that in the reception and the last ponds, B1 and B7 respectively, the temperature rates increase were the lowest. This fact is related to the relatively important depth of these ponds (1.75 m) almost filled with OMW. Furthermore, the temperature varied between 25 and 43°C in the three intermediate ponds (B4, B5 and B6). There are significant changes of temperature in the ponds B1, B4, B5 and B6 but no significant variation was found in the last pond ($P > 0.05$).

Temperature and natural evaporation have an important effect on hydrodynamic and biochemical processes in evaporation ponds. Indeed, they cause a thermal stratification, warming the superficial water layers and increasing gradually the OMW density from the top to the bottom (Tadesse et al. 2004). The gradient of temperature with depth inside the

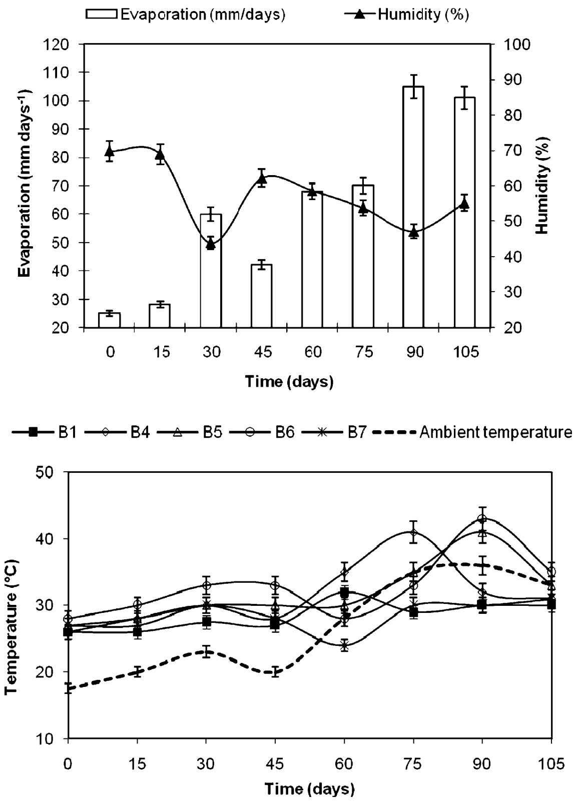

Fig. 3 Evolution of temperature, evaporation and relative humidity

evaporation ponds, will select the type of microrganisms that will grow and survive in this environment (Williams 1998).

In semi arid regions, evaporation ponds which are a conventional means for wastewater disposal, minimize the risk of ground or surface water contamination. The success of wastewater disposal by evaporation, requires that the water input in the system, including precipitation, is less, or at least equal to the effective volume evaporated from the pond. The net evaporation may be defined as the difference between the evaporation and the precipitation during any time period. Evaporation rates are to a great extent dependent upon the characteristics of the water body. The wastewater evaporation in ponds aimed the reduction of the final sludge volume, and hence water temperature will influence the evaporation rates. However, the low value of saturation vapor pressure in the air will limit the evaporation rates (Cheremisinoff 2002).

pH, humidity and total phosphorus

Table 4 shows the variation of pH, humidity and total phosphorus. In all the ponds (B1 to B7), pH values decreased from approximately 5.0 to 4.0, reflecting the initial acidic OMW and also its acidic degradative metabolism by microbial biota during the storage. The comparison of these values showed a difference less than 5%. This confirms a homogenized acidification process specifically related to operation time. The pH modification is also dependent on the diurnal cycle of sunlight intensity (Tadesse et al. 2004).

During the storage, the OMW humidity decreased in all evaporation ponds. The initial humidity rose progressively from around 96 to 92%, especially after 2 months storage when a relatively important decrease was registered in ponds B4 and B5, and humidity fall down to 75 and 73% respectively. The humidity variation affects the composition and the dynamics of microbial population. Humidity was linearly and significantly correlated with fungal and microbial flora (Cuevas 1995; De Man 1999).

During the first month, the total phosphorus concentration showed a slight increase in B1, B4 and B5; it then decreased during the last storage period. Two processes can take place in evaporation ponds: biological assimilation and chemical precipitation. The total phosphorus progress in the 4 studied ponds was similar with a notable concentration reduction from one pond to another. Under aerobic condition and acidic environment, soluble phosphorus is easily assimilated by aerobic bacteria. However, in anaerobic conditions, the presence of volatile fatty acids (VFA) readily biodegradable compounds, mobilize some phosphorus for polymerisation, at the expense of energy from polyphosphate breakdown. Poly-β-hydroxybutyric acid (PHB) plays an important role in the previously mentioned mechanism. The presence of PHB in biopolyphosphate bacteria enhances the growth of these microorganisms and the synthesis of their own polyphosphate by using available soluble phosphate, and hence, PHB and polyphosphate will play a mutually interdependent role managing aerobic bacteria to survive through an anaerobic period (Mara and Horan 2003).

BOD_5/COD, polyphenols, phenols

The evolution of BOD_5/COD, polyphenols and phenols concentration is represented in Fig. 4.

The BOD_5/COD ratio showed a fluctuation explained by variability of the OMW during storage. However, the BOD_5/COD ratios remained relatively high and exceeding 20%, value required for effluent biological treatment. As a result, in spite of the relatively high evaporation, the OMW remained biodegradable (Ammar and Ueno 1999). The BOD_5/COD ratio increased at 45 days and it then decreased until days 105 in B4 and B5 but it showed fluctuations in B1, B6 and B7. In all the studied ponds, the rainfall didn't affect the studied parameters. However, it afected BOD_5/COD ratios which increased. The highest BOD_5/COD ratio values were found in the 2 last ponds B6 and B7, these varied between 0.27 and 0.41 reflecting the microbial ability on OMW degradation (Ammar and Ueno 1999). Similar results were found by Paredes et al. (1999), who showed low OMW organic matter mineralization degree during its storage in the evaporation ponds.

In OMW facultative ponds, the biodegradation of organic matter is stabilized by both anaerobic and aerobic processes. In deep ponds, the anaerobic processes convert organic matter in methane and carbon dioxide. However, in aerated surface, the metabolism reduces compounds produced in anaerobic layer, minimizing odor release and oxidizing soluble oxygen-demanding compounds (Leslie Grady et al. 1999).

The polyphenols rates increased in all the studied ponds, while, phenol concentrations decreased. In ponds B1, B4, B5 and B6, the polyphenols concentrations increased from 11 g l^{-1} to 29, 27, 24 and 20 g l^{-1} respectively. This noticeable phenol concentration, becomes a major environmental problem especially because of the national and the European standards limiting phenols in wastewater (<1 mg l^{-1}) (JICA 1993; Torrecilla et al. 2007). The polyphenols and phenol evolutions were significantly different while comparing the progress in all the earlier ponds (B1–B6) to the last pond (B7). In evaporation ponds, the initial redish color of fresh OMW became black after storage under sun light oxidation. The presence of lignin and its derivates, polymerized tannins,

Table 4 Evolution of pH and humidity

Pond	Storage time (days)	pH	Humidity (%)	Total phosphorus (mg l^{-1})
B1	1	4.93 ± 0.02	95.00 ± 0.40	803.00 ± 2.00
	15	4.89 ± 0.01	95.00 ± 0.30	954.00 ± 13.00
	30	4.78 ± 0.02	91.40 ± 0.60	1024.00 ± 32.00
	45	4.38 ± 0.03	94.80 ± 0.20	999.00 ± 1.00
	60	4.20 ± 0.01	91.60 ± 0.40	912.00 ± 2.00
	75	4.10 ± 0.02	90.00 ± 0.30	852.00 ± 12.00
	90	4.00 ± 0.03	88.00 ± 0.70	740.00 ± 5.00
	105	4.20 ± 0.02	79.00 ± 1.00	701.00 ± 8.00
B4	1	4.87 ± 0.01	94.50 ± 0.50	705.00 ± 12.00
	15	4.61 ± 0.01	95.00 ± 0.20	75.00 ± 8.00
	30	4.70 ± 0.02	92.50 ± 0.20	801.00 ± 7.00
	45	4.40 ± 0.03	93.80 ± 0.20	633.00 ± 10.00
	60	4.30 ± 0.01	92.60 ± 0.40	600.00 ± 13.00
	75	4.40 ± 0.02	91.70 ± 0.30	584.00 ± 6.00
	90	4.30 ± 0.04	85.90 ± 0.10	498.00 ± 2.00
	105	4.10 ± 0.03	75.00 ± 0.60	431.00 ± 8.00
B5	1	4.84 ± 0.02	94.49 ± 0.51	615.00 ± 12.00
	15	4.58 ± 0.01	95.60 ± 0.40	635.00 ± 13.00
	30	4.50 ± 0.01	92.70 ± 0.30	687.00 ± 11.00
	45	4.50 ± 0.02	92.20 ± 0.30	503.00 ± 9.00
	60	4.20 ± 0.02	92.00 ± 0.60	426.00 ± 15.00
	75	3.90 ± 0.03	86.00 ± 0.50	398.00 ± 11.00
	90	4.00 ± 0.04	85.00 ± 0.40	361.00 ± 4.00
	105	4.10 ± 0 .02	73.00 ± 0.30	307.00 ± 6.00
B6	1	4.86 ± 0.01	96.30 ± 0.70	499.00 ± 6.00
	15	4.76 ± 0.02	96.00 ± 0.33	431.00 ± 6.00
	30	4.60 ± 0.03	93.67 ± 0.80	365.00 ± 5.00
	45	4.20 ± 0.01	94.20 ± 0.50	279.00 ± 4.00
	60	4.00 ± 0.02	94.20 ± 0.20	264.00 ± 4.00
	75	4.10 ± 0.02	94.80 ± 0.50	251.00 ± 5.00
	90	4.00 ± 0.03	94.20 ± 0.20	198.00 ± 9.00
	105	4.10 ± 0.02	90.80 ± 0.40	136.00 ± 4.00
B7	1	4.50 ± 0.02	96.70 ± 0.50	385.00 ± 7.00
	15	4.40 ± 0.03	96.60 ± 0.20	301.00 ± 3.00
	30	4.10 ± 0.04	94.50 ± 0.40	274.00 ± 2.00
	45	4.00 ± 0.03	96.00 ± 0.30	242.00 ± 4.00
	60	3.90 ± 0.02	95.40 ± 0.30	206.00 ± 3.00
	75	3.90 ± 0.01	96.70 ± 0.60	187.00 ± 2.00
	90	4.00 ± 0.03	96.70 ± 0.40	164.00 ± 1.00
	105	3.90 ± 0.02	96.40 ± 0.30	109.00 ± 1.00

causes oxidation which turns the OMW color to dark brown (Verenich et al. 2005). However, Niaounakis and Halvadakis (2006) showed that the red color observed on the surface on the OMW storage—ponds may be caused by copper oxide (Cu_2O). Several processes can be involved in polyphenols and phenols evolution in ponds such as: polymerization, biodegradation (Beccari et al. 2002; Chtourou et al. 2004),

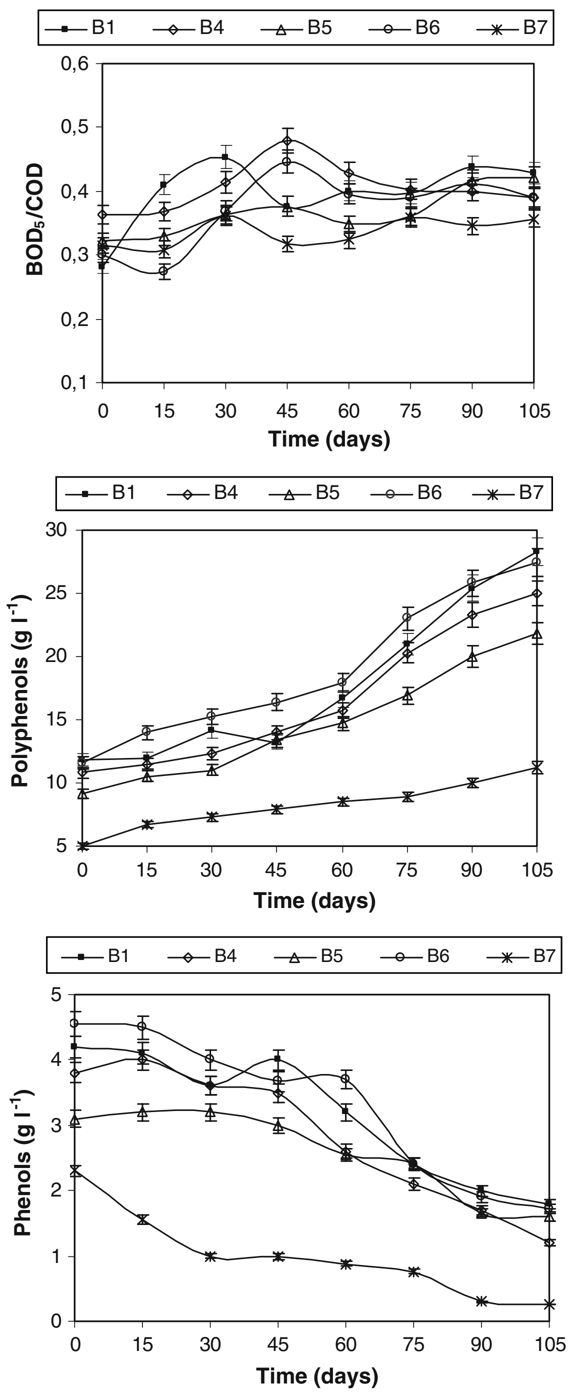

Fig. 4 Evolution of BOD_5/COD, polyphenols and phenols

volatilization of some compounds and physical and/or chemical soil-particles adsorption (Jarboui et al. 2008; Rana et al. 2003; Santi et al. 2008). Phenolic compounds are known by their phytotoxicity and antibacterial properties (Saez et al. 1992; Chtourou et al. 2004; Quaratino et al. 2007; Sierra et al. 2001). Paixao et al. (1999) proved that the high-toxicity of OMW, was independent of the extraction procedure used and they emphasized the difficulties in determining the OMW chemical parameters causing the toxicity.

Microbiological flora evolution

Figure 5 shows the ratios evolution of moulds/bacteria, yeasts/bacteria and moulds/yeasts.

The ratios of moulds/bacteria and yeasts/bacteria were comparable with an increase of yeasts and moulds after 75 days of storage in all the ponds (B4–B7). The moulds/bacteria and yeasts/bacteria ratios increased significantly from 0.9 to 2.1 and from 1 to 2.4 in B4 and from 0.8 to 1.3 and 0.9 to 1.4 in the last pond (B7), respectively. However, the moulds/yeasts ratio remained constant in all the ponds, with value around 0.8. The relatively high values of moulds/bacteria and yeasts/bacteria ratios monitored during the last storage month reflected a physico-chemical variation occurring in the ponds, allowing acidic flora to grow. Furthermore, the pH progress confirmed such acidification (Table 4). The decrease of bacterial populations could be also attributed to the OMW antibacterial activity resulting from higher concentration of polyphenolic compounds. Indeed, Shapton and Shapton (1998) mentioned that environment pH values may cause growth rate decrease and a sensitivity increase to other inhibitory factors when values apart from the optimum. Moreover, water activity is a factor with major selective influence on microbial growth, and is therefore of great importance in the environmental microbial ecology. A growth reduction occurs when water activity is reduced in various organic materials. Indeed, fresh organic matter with water activity values above 0.95 is rapidly spoiled. At such water activity range, bacteria outgrow yeasts and moulds, as their metabolic rates are generally higher and they compete successfully for available nutrients and space. In evaporated organic matter, water activity is in the range of 0.95–0.90 and bacteria are still the dominating flora, but nutritionally fastidious types such as Gram-negative rods and spore-forming bacteria progressively loose to lower water activity tolerant cocci and lactobacilli. Then, yeasts and moulds become the

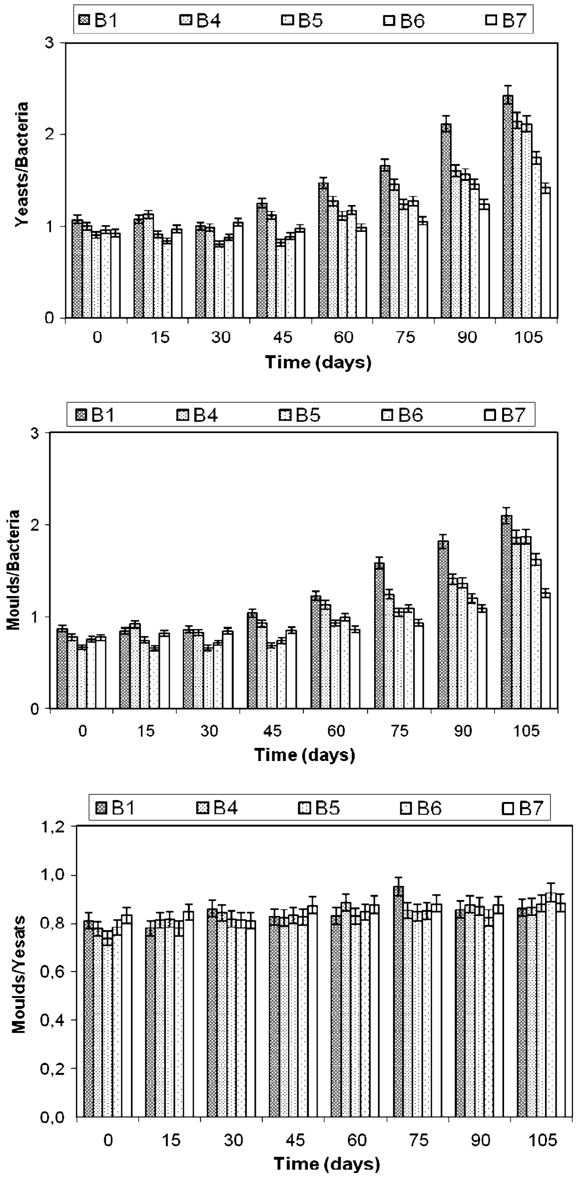

Fig. 5 Ratios evolution of moulds/bacteria, yeasts/bacteria and moulds/yeasts

dominant organisms with minimum water activities growth of approximately 0.88 and 0.75 respectively. In a low water activity environment, microorganisms must adapt or die. A part of their adaptation is a thermodynamically adjustment by lowering their internal water activities, to regain hypertonicity in relation to the surrounding medium (Shapton and Shapton 1998). The water activity affects the growth of some soil isolates bacteria such as *Clostridium* and *Bacillus* that vary respectively from 0.94 to 0.95 and from 0.95 to 0.98. Yeasts water activity in *Saccharomyces* and *Zygosaccharomyces* vary between 0.80 and 0.90. For moulds, the water activity growth is ranged from 0.70 to 0.80 and from 0.77 to 0.83 respectively for *Aspergillus* and *Penicillium* (Christian 2000). These strains and others were used in biological treatment of OMW (Chtourou et al. 2004; Gharsallah 1993; Ramos-Cormenzana et al. 1996). Nevertheless, Amaral et al. (2008) showed the high number of filamentous fungi and yeasts in OMW and mentioned that the population of filamentous fungi and yeasts were very similar in abundance both in olive centrifuge water (OCW) and OMW samples. The same authors showed the low heterotrophic bacteria concentrations in the same study.

Fungi enzymes are well known for providing them resistance and tolerance to high polyphenolic compounds concentration. A variety of proteins with interesting biological activities is synthesized by fungi and many of these have potential applied activities, such as OMW biodegradation (Chtourou et al. 2004; Laconi et al. 2007).

Tardioli et al. (1997) mentioned the presence of *Penicillum, Cyclopium* and *Geotrichum* fungal species in OMW contaminated soils. Over the total isolated, these represented 40–80, 0–43 and 0–45% respectively. Furthermore, Chtourou et al. (2004) and Giannoutsou et al. (2004) showed the fungi abilities to degrade sugars, lipids and polyphenols available in OMW.

Microorganisms metabolize organic substances dissolved in water and transform them into carbonic acid, water and biomass by enzymatic reactions. The major types of enzymes involved in wastewaters biochemistry degradation are oxidation, reduction, hydrolysis, deamination and decarboxylation (Gray 2005). In open ponds, the suitable microorganisms for wastewater purification grow independently. Two types of microorganisms may be found suspended organisms floating in the water, and sessile organisms, which often form biofilms on stones (Madrid et al. 2000). The microbial populations in industrial stabilization ponds present higher diversity than the ones in municipal stabilization ponds. The predominant bacteria will depend on the industrial chemicals in the wastewater (Mc Kinney 2004). The aerobic conditions in the stabilization ponds allow the bacteria to grow aerobically, especially in the upper layers where *Zooglea, Pseudomonas, Chromobacter,* *Achromobacter, Alcaligenes and Flavobacterium* are active and *Escherichia coli* and *Nocardia* perform less well than others in removing carbonaceous pollution (Ammar and Ueno 1999). Facultative obligeate and anaerobic species are susceptible to be found in the anoxic or anaerobic zone, these bacteria include sulfate-reducing bacteria, facultative aerobic bacteria (fermentate) and methanogenic bacteria. Some bacteria in the anaerobic zone are capable of fermentation (*Aeromnas*, *Citrobacter*, *Proteus* and *Serratia*). They produce and accumulate organic compounds such as lactic acid, succinic acid, propionic acid, butyric acid and ethanol during fermentation. Besides bacteria, *Fusarium, Geotrichum* and *Trichosporium* were identified over a 100 species of fungi in the biomass of biological aerobic purification. Protozoa and Metazoa are also common in aerobic treatment process (Mara and Horan 2003).

Conclusion

The desorption isotherms of OMW were determined at 30°C and different water activities. The isotherms showed the influence of water activity and the RH on the OMW storage. The desorption isotherm was a sigmoidal curve corresponding to type II. The relationship between the EMC and water activity was described by GAB and Peleg models with a high coefficient correlation. The OMW evaporation was confirmed by the increases of the majority of physicochemical parameters. While others parameters such as phenols and total phosphorus were decreased with microbial biomass evolution. The water activity is a major selective factor, which influenced the development of several microorganisms (bacteria, yeasts and moulds). The growth of specific microbial flora constituted an important factor for the bioremediation of OMW organic compounds and indicated the viability and the dynamic of the stabilization ponds, where established models describing evaporation would help in predicting the state of the dehydration.

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