ELSEVIER

Bioresource Technology 67 (1999) 111–115

BIORESOURCE TECHNOLOGY

Characterization of olive mill wastewater (alpechin) and its sludge for agricultural purposes

C. Paredes*, J. Cegarra, A. Roig, M.A. Sánchez-Monedero, M.P. Bernal

Department of Soil and Water Conservation and Organic Waste Management, Centro de Edafología y Biología Aplicada del Segura, CSIC, PO Box 4195, 30080 Murcia, Spain

Received 1 May 1998; revised 22 May 1998; accepted 27 May 1998

Abstract

Ten samples of olive mill wastewater (OMW) taken from different mills in southern Spain and other ten of OMW sludges from evaporation ponds were analysed. The aim was to study the composition of these wastes and to find relationships which would make it possible to use easily determinable parameters to ascertain their composition.

Compared with other organic wastes, these materials had a high potassium concentration, a similar organic matter content and notable levels of nitrogen, phosphorus, calcium, magnesium and iron. The highest potassium concentrations were observed in the OMWs, while the sludges showed higher levels of the other nutrients, especially iron. The dry matter of the OMWs was significantly correlated with most of the parameters studied but, in the sludges, the only correlation was between the ash content and the total organic carbon and total nitrogen concentrations. The regression equations obtained permitted a rapid characterization of the OMWs from their dry matter content.

Keywords: Olive-mill wastewater; Sludge; Organic carbon; Plant nutrients; Fats; Polyphenols; Carbohydrates

1. Introduction

Olive oil extraction produces vast amounts of liquid and solid wastes. The elimination of olive mill wastewater (OMW) is one of the main environmental problems related to the olive oil industry in Mediterranean countries, where Spain and Italy are the greatest producers. During recent years, the OMW production of Spain has been approximately 2.1×10^6 m^3 $year^{-1}$, which is generated during a few months of the year (November–February). This liquid waste comes from the vegetable water of the fruit and the water used in the different steps of oil production and contains olive pulp, mucilage, pectin, oil, etc. suspended in a relatively stable emulsion.

To solve the problems associated with OMW, different elimination methods have been proposed based on evaporation ponds, thermal concentration and physico-chemical and biological treatments, as well as its direct application to agricultural soils as an organic fertilizer (Fiestas Ros de Ursinos and Borja Padilla, 1992; Martínez Nieto and Garrido Hoyos, 1994). However, the most frequently used methods nowadays are the direct application to agricultural soils and storage in evaporation ponds, which produces a sludge.

OMW contains a high organic load, substantial amounts of plant nutrients and is a low cost source of water (Cegarra et al., 1997), all of which favour its use as a soil fertilizer. However, many authors have observed phytotoxic effects in plants when this waste is used directly as an organic fertilizer and have therefore warned against its direct application (Zucconi and Bukovac, 1969; Jelmini et al., 1976). Such negative effects are associated with its high mineral salt content, low pH and the presence of phytotoxic compounds, especially phenols. Negative effects have also been recorded on soil properties, including the immobilization of available nitrogen (Pérez and Gallardo-Lara, 1987; Saviozzi et al., 1991), the displacement of the exchange complex calcium by potassium in an anfisol, increased salinity (López et al., 1996) and decreased plant-available magnesium, perhaps because of the antagonistic effect of potassium (Pérez et al., 1986).

Therefore, before an OMW can be used properly and safely it must be characterized. The aim of the

---

*Corresponding author.

0960-8524/99/$ — see front matter
PII: S0960-8524(98)00106-0

study described in this paper was to characterize OMW and OMW-sludge samples from different mills in southern Spain in an attempt to find relationships which would make it possible to estimate the composition of these wastes from easily determined parameters.

2. Methods

Ten OMW samples were collected directly from the centrifuge of different mills in southern Spain and the ten OMW sludges from different evaporation ponds. All the samples were homogenized in a mixer and stored in a cool environment (4°C) prior to analysis. Electrical conductivity (EC) and pH were determined directly in the OMW samples and in a 1:5 (w/v) water-soluble extract of the OMW sludge samples, density (*d*) by weighing an exactly measured volume of OMW, dry matter content (DM) by drying at 105°C for 12 h, organic matter (OM) by loss on ignition at 430°C for 24 h (Navarro et al., 1993) and total nitrogen (TN) and total organic carbon (TOC) by automatic microanalysis (Navarro et al., 1991). After $HNO_3/HClO_4$ digestion, the P content was measured colorimetrically (Kitson and Mellon, 1944), Na and K by flame photometry and Ca, Mg, Fe, Cu, Mn and Zn by atomic absorption spectrophotometry. Polyphenols were extracted with ethyl acetate (Balice and Cera, 1984) and determined by the Folin method (Maestro Durán et al., 1991), carbohydrates by the anthrone method (Brink et al., 1960) after deproteinizing the sample with $Pb(CH_3-COO)_2$ (Ebell, 1969) and fats by extraction with petroleum ether (Ministerio de Sanidad y Consumo, 1985). These methods for phenols, carbohydrates and fats were not suitable for determination on sludges.

3. Results and discussion

3.1. *Characteristics of the olive oil industry wastes*

The analyses made of OMW and OMW sludge samples are summarized in Table 1. As was to be expected, the percentage of dry matter of OMW sludges was statistically higher than that of OMWs, while no significant differences were observed in the pH, EC, OM and TOC between the sludges and the OMWs. The similar OM and TOC values might indicate the low degree of mineralization suffered by the organic matter of OMW during its storage in the evaporation ponds, while simultaneous processes of degradation and reorganisation may have taken place during this time. This was suggested by Saiz-Jiménez et al. (1986), who observed the simultaneous degradation of high molecular weight fractions to produce fractions of a smaller molecular weight and the synthesis of compounds which were more resistant to degradation. Pérez et al. (1992) also pointed to the lower phenol

Table 1
Analysis of OMW and OMW sludge samples (dry weight)

	OMWs			OMW sludges		
	Mean	Range	CV	Mean	Range	CV
Dry matter (%) [a]	7.19 **b**	4.12–16.38	3.87	48.00 **a**	14.23–94.69	43.38
pH	5.17 **a**	4.80–5.50	4.83	5.41 **a**	4.85–5.87	7.86
EC (dS/m)	5.50 **a**	4.00–13.98	41.73	6.74 **a**	1.53–9.03	53.76
OM (%)	64.60 **a**	58.45–70.63	6.33	71.06 **a**	43.84–94.26	26.43
TOC (%)	47.52 **a**	43.61–53.45	6.46	47.90 **a**	31.08–63.21	25.73
TN (%)	0.88 **b**	0.58–1.13	25.18	1.74 **a**	0.60–2.73	38.92
P (%)	0.19 **a**	0.06–0.32	51.73	0.14 **a**	0.06–0.30	45.37
K (%)	5.24 **a**	3.30–6.94	23.18	1.41 **b**	0.78–3.10	57.85
Na (%)	0.15 **a**	0.04–0.48	114.97	0.06 **a**	0.02–0.13	63.71
Ca (%)	0.42 **b**	0.32–0.53	18.66	2.87 **a**	0.51–10.22	107.24
Mg (%)	0.18 **b**	0.06–0.22	26.10	0.36 **a**	0.09–0.67	52.44
Fe (mg/Kg)	951 **b**	652–1482	31.83	4501 **a**	394–12096	97.74
Cu (mg/Kg)	21 **b**	14–44	40.63	61 **a**	14–203	91.51
Mn (mg/Kg)	15 **b**	1–53	110.07	97 **a**	19–288	91.15
Zn (mg/Kg)	57 **a**	31–82	31.55	37 **b**	18–55	37.30
d (g/cm^3)	1.02	1.01–1.06	1.30	nd	nd	nd
Fats (%)	4.27	0.55–11.37	84.41	nd	nd	nd
Polyphenols (%)	2.21	1.32–3.99	35.80	nd	nd	nd
Carbohydrates (%)	12.22	3.37–32.91	76.79	nd	nd	nd

[a] Referred to fresh weight.
CV: Coefficient of variation. nd: Not determined (see Section 2).
Mean values followed by the same letter are not significantly different ($p < 0.05$) between the groups of wastes.

Table 2
Correlation matrix between the main analytical parameters of OMW samples referred as fresh weight ($n = 10$)

	Dry matter (g/l)	Ash (g/l)	EC (dS/m)	d (g/cm3)	TOC (g/l)	TN (g/l)	P (g/l)	K (g/l)	Ca (g/l)	Fe (mg/l)	Cu (mg/l)	Mn (mg/l)	Zn (mg/l)	Fats (g/l)	Poly-phenols (g/l)
Ash	0.982***	1													
EC	0.968***	0.972***	1												
d	0.967***	0.928***	0.948***	1											
TOC	0.995***	0.978***	0.956***	0.950***	1										
TN	0.877***	0.873***	0.857**	0.783**	0.909***	1									
P	0.876***	0.933***	0.911***	0.772**	0.883***	0.867***	1								
K	0.937***	0.969***	0.975***	0.904***	0.925***	0.800**	0.914***	1							
Ca	0.890***	0.824**	0.824**	0.867***	0.893***	0.845**	0.690*	0.726*	1						
Fe	0.869***	0.840**	0.783**	0.819**	0.878***	0.771**	0.697*	0.763**	0.795**	1					
Cu	NS	NS	0.676*	NS	NS	NS	0.689*	NS	NS	NS	1				
Mn	0.762**	0.835**	0.792**	0.697*	0.734*	NS	0.772**	0.878***	NS	NS	NS	1			
Zn	0.911***	0.908***	0.915***	0.916***	0.897***	0.719*	0.824**	0.917***	0.650*	0.767**	0.632*	0.768**	1		
Fats	0.795**	0.816**	0.733*	0.694*	0.827**	0.769**	0.731*	0.798**	NS	0.854**	NS	0.713*	0.748**	1	
Polyphenols	0.925***	0.962***	0.918***	0.858**	0.928***	0.810**	0.897***	0.965***	0.724*	0.857**	NS	0.856**	0.875***	0.905***	1
Carbohydrates (g/l)	0.728*	0.734*	0.678*	0.761**	0.728*	NS	0.653*	0.684*	NS	0.694*	NS	NS	0.808**	NS	0.708*

*, **, ***: Significant at $p < 0.05$, 0.01, 0.001, respectively. NS: Not significant.
Data not shown were not statistically significant.

content of an OMW stored in an evaporation pond compared with that of a fresh OMW, and suggested that this may have been due to the polymerization of the low molecular weight phenols.

As regards the macronutrient content, the sludges had higher levels of TN, as has been reported previously by Saiz-Jiménez et al. (1986) in a study to identify proteins in OMW and OMW sludge. This might have been due to the biological fixation of nitrogen during storage of OMW in evaporation ponds since OMW is considered by many authors to be suitable substrate for the growth of free nitrogen fixers (Paredes et al., 1987; García-Barrionuevo et al., 1992).

The levels of K were lower in the sludges than in the OMWs, probably because of the highly soluble nature of this element, which would lead to its filtering through the permeable substrate in the bottom of the ponds. The higher Ca levels noted in the sludges may have been due to mixing with the calcium present in the soil where the ponds were constructed, since the soils of southern Spain are calcareous.

The levels of micronutrients varied greatly although they were generally higher in the sludges. The high iron content of the sludges may, as in the case of Ca, have been due to mixing with the mineral components in the bottom of the ponds.

The fat, polyphenol and carbohydrate contents and density of OMW were also determined (Table 1), the fat and carbohydrate levels, particularly, varying greatly.

The two groups of wastes analysed generally showed high concentrations of K, similar quantities of OM and

Table 3
Correlation matrix between the main analytical parameters of OMW sludge samples referred as dry weight ($n = 10$)

	Dry matter (%)	Ash (%)	pH	EC (dS/m)	TOC (%)	TN (%)	Mg (%)	Fe (mg/Kg)
pH	0.683*	0.648*	1					
EC	NS	0.696*	NS	1				
TOC	NS	−0.942***	−0.773**	NS	1			
TN	NS	−0.906***	−0.708*	NS	0.918***	1		
P	NS	0.652*	NS	NS	NS	NS		
Ca	NS	0.697*	0.636*	NS	−0.723*	NS		
Fe	NS	NS	NS	NS	NS	NS	0.813**	1
Cu	NS	NS	NS	−0.678*	NS	MS	0.658*	NS
Mn	NS	NS	NS	NS	NS	NS	NS	0.663*
Zn (mg/Kg)	NS	0.884***	NS	NS	−0.850**	−0.764**	NS	NS

*, **, ***: Significant at $p < 0.05$, 0.01, 0.001, respectively. NS: Not significant.
Data not shown were not statistically significant.

Table 4
Parameters of the linear regression and correlation coefficient values between dry matter (DM) and electrical conductivity (EC), organic matter (OM), total organic carbon (TOC), the main macro and micronutrients and polyphenols in OMW. $Y = a + bX$; X = DM (g/l). ($n = 10$)

Y	a	b	r
EC (dS/m)	1.516*	0.071***	0.9682***
Ash (g/l)	−4.798 NS	0.427***	0.9822***
TOC (g/l)	1.220 NS	0.455***	0.9952***
TN (g/l)	0.160 NS	0.006***	0.8764***
P (g/l)	−0.081 NS	3.237***	0.8756***
K (g/l)	−0.916 NS	0.066***	0.9365***
Ca (g/l)	0.080 NS	3.074***	0.8898***
Fe (mg/l)	16.994 NS	0.667**	0.8686***
Zn (mg/l)	−0.701 NS	0.068***	0.9114***
Polyphenols (g/l)	−1.438*	0.044***	0.9247***

*, **, ***: Significant at $p < 0.05$, 0.01, 0.001, respectively. NS: Not significant.

notable levels of N, P, Ca, Mg and Fe compared with those found by Cegarra et al. (1993) in manures and composts made from municipal solid wastes, which are commonly used as organic fertilizers. According to that, these wastes from the olive oil industry could be used as organic fertilizers in agricultural soils both for their elimination and for improvement of soil fertility. However, the notable contents of mineral salts, fats and polyphenols in OMW could limit their direct application to soils.

3.2. Relationships between the main analytical parameters of OMW and OMW sludge samples

The great variation found in the characteristics of these wastes (see coefficients of variation, Table 1), means that they should be characterized fully before being used for agricultural purposes. This is particularly true in the case of the sludges since their composition depends not only on the factors which influence the composition of OMW but on such factors as the time of storage, depth of the pond (which decides whether the organic matter degrades aerobically or anaerobically), climatic conditions, loss through seepage, etc. However, since a full analysis would be very time consuming, it would be useful to establish equations which would make it possible to ascertain most parameters from one of them easily determined.

Table 5
Parameters of the linear regression and correlation coefficient values between ash and total organic carbon (TOC) and total nitrogen (TN) in OMW sludges. $Y = a + bX$; X = Ash (%) (dry weight). ($n = 10$)

Y	a	b	r
TOC (%)	65.784***	−0.618***	−0.9418***
TN (%)	2.682***	−0.033***	−0.9060***

***: Significant at $p < 0.001$.

Correlations between the main parameters of the OMWs, referred to fresh weight, are shown in Table 2, where those between dry matter and ash, EC, *d*, TOC, principal nutrients and polyphenols are highly statistically significant ($p < 0.001$). However, in the case of the sludges significant correlations ($p < 0.001$) were found only between ash and TOC, TN and Zn and between TOC and TN (Table 3).

Table 4 shows the values for the coefficient of correlation and of the parameters of the regression equations obtained between dry matter and EC, ash, TOC, principal nutrients and polyphenols for the OMWs, while Table 5 shows the regression equations between ash and TOC and TN for OMW sludges. In both groups of equations the high *r* values, of between 0.9952 and 0.8686, indicate a high level of correlation ($p < 0.001$). In the case of the OMWs, it was found that, except for EC and polyphenols, the intercept (*a*) was not statistically significant so that the ash, TOC, TN, P, K, Ca, Fe and Zn contents could be determined by multiplying the concentration of dry matter by the slope (*b*). In the case of the sludges, on the other hand, the intercept (*a*) was significant for all parameters so that an equation must be used to calculate the concentration of TOC and TN from the ash content.

3.3. Conclusions

Both groups of wastes showed generally notable contents of organic matter and substantial quantities of plant nutrients compared with those found in manures and city refuse composts.

The great variation in most of the parameters determined in both the OMWs and the sludges means that they should be characterized fully before they are used for agricultural purposes. In the case of the OMW, their composition can be easily ascertained by determining the dry matter content, using the highly significant correlations observed between this parameter and the ash, EC, principal nutrients and polyphenols. In the case of OMW sludges, only the TOC and TN concentrations can be calculated by reference to the ash content, a routine method which is much more straightforward and less costly than those usually used for their analysis.

Acknowledgements

This research was carried out in the framework of EU contract No. EVWA-CT 92-0006.

References

Balice, V., Cera, O., 1984. Acidic phenolic fraction of the olive vegetation water determined by a gas chromatographic method. Grasas Aceites 35, 178–180.

Brink, R.H., Dubach, P., Lynch, D.L., 1960. Measurement of carbohydrates in soil hidrolizates with anthrone. Soil Sci. 89, 157–166.

Cegarra, J., Paredes, C., Roig, A., Bernal, M.P., García, D., 1997. Use of olive mill wastewater compost for crop production. Int. Biodeter. Biodegr. 38, 193–203.

Cegarra, J., Roig, A., Navarro, A.F., Bernal, M.P., Abad, M., Climent, M.D., Aragón, P. 1993. Características, compostaje y uso agrícola de residuos sólidos urbanos. Paper presented at Jornadas de Recogidas Selectivas en Origen y Reciclaje, Córdoba (Spain).

Ebell, L.F., 1969. Variation in total soluble sugars of conifer tissues with method of analysis. Phytochemistry 8, 227–233.

Fiestas Ros de Ursinos, J.A., Borja Padilla, R., 1992. Use and treatment of olive mill wastewater: Current situation and prospects in Spain. Grasas Aceites 43, 101–106.

García-Barrionuevo, A., Moreno, E., Quevedo-Sarmiento, J., González-López, J., Ramos-Cormenzana, A., 1992. Effect of wastewaters from olive oil mills (alpechin) on *Azotobacter* nitrogen fixation in soil. Soil Biol. Biochem. 24, 281–283.

Jelmini, M., Sanna, M., Pelosi, N., 1976. Indagine sulle acque di rifiuto degli stabilimenti di produzione olearia in provincia di Roma: possibilitá di depurazione. Ind. Aliment.-Italy 15,(11), 123–131.

Kitson, R.E., Mellon, M.G., 1944. Colorimetric determination of P as a molybdovanadato phosphoric acid. Ind. Eng. Chem. Anal. Ed. 16, 379–383.

López, R., Martínez-Bordiú, A., Dupuy de Lome, E., Cabrera, F., Sánchez, M.C., 1996. Soil properties after application of olive oil mill wastewater. Fresenius Envir. Bull. 5, 49–54.

Maestro Durán, R., Borja Padilla, R., Martín Martín, A., Fiestas Ros de Ursinos, J.A., Alba Mendoza, J., 1991. Biodegradación de los compuestos fenólicos presentes en el alpechín. Grasas Aceites 42, 271–276.

Martínez Nieto, L., Garrido Hoyos, S.E., 1994. El alpechín. Un problema medioambiental en vías de solución (I). Quibal 41, 755–765.

Ministerio de Sanidad y Consumo, 1985. Análisis de Alimentos. Métodos Oficiales Recomendados por el Centro de Investigación y Control de la Calidad. Madrid.

Navarro, A.F., Cegarra, J., Roig, A., Bernal, M.P., 1991. An automatic microanalysis method for the determination of organic carbon in wastes. Commun. Soil Sci. Plant Anal. 22, 2137–2144.

Navarro, A.F., Cegarra, J., Roig, A., García, D., 1993. Relationships between organic matter and carbon contents of organic wastes. Biores. Technol. 44, 203–207.

Paredes, M.J., Moreno, E., Ramos-Cormenzana, A., Martínez, J., 1987. Characteristics of soil after pollution with waste waters from olive oil extraction plants. Chemosphere 16, 1557–1564.

Pérez, J., De la Rubia, T., Moreno, J., Martínez, J., 1992. Phenolic content and antibacterial activity of olive oil waste waters. Environ. Toxicol. Chem. 11, 489–495.

Pérez, J.D., Esteban, E., Gallardo-Lara, F., 1986. Direct and delayed influence of vegetation water on magnesium uptake by crops. Paper presented at International Symposium on Olive by Products Valorization, Sevilla (Spain).

Pérez, J.D., Gallardo-Lara, F., 1987. Effects of the application of wastewater from olive processing on soil nitrogen transformation. Commun. Soil Sci. Plant Anal. 18, 1031–1039.

Saiz-Jiménez, C., Gómez-Alarcón, G., de Leeuw, J.W., 1986. Chemical properties of the polymer isolated in fresh vegetation water and sludge evaporation ponds. Paper presented at International Symposium on Olive by Products Valorization, Sevilla (Spain).

Saviozzi, A., Levi-Minzi, R., Riffaldi, R., Lupetti, A., 1991. Effetti dello spandimento di acque di vegetazione sul terreno agrario. Agrochimica 35, 135–148.

Zucconi, F., Bukovac, N.J., 1969. Analisi sull'attivitá biologica delle acque di vegetazione delle olive. Riv. dell'Ortoflorofrutticoltura Italiana 53, 443–461.