Potential Environmental Impact of Effluents from the Artichoke (*Cynara scolymus* L.) Byproduct Ensiling Process Using Additives

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Three treatments have been tested on canned artichoke byproduct after 50 days of ensilage: formic acid at 20% in doses of 2 mL·kg⁻¹ (FA), cane sugar molasses at 50 g·kg⁻¹ (M), and sodium chloride at 30 g·kg⁻¹ (SC). A fourth batch acted as a control group (C). The nutritive value, fermentation characteristics, environmental pollution effect, and total volume of effluents released have been studied. The highest nutritive value recorded was with SC silage. The use of the additives did not significantly improve the fermentation stability of the silage, but the total production of effluents in each treatment–52.7 (FA), 46.9 (M), and 55.2 (SC)—was significatly lower (P < 0.01) than that of the control group (70.1 L·Tm⁻¹). The chemical oxygen demand (COD), 117300 mg of O₂·L⁻¹, and the conductivity, 46.4 $\mu\Omega^{-1}$ ·cm⁻¹, were significantly higher (P < 0.01) in M and SC, respectively, than in the other group.

Keywords: Artichoke; effluent; byproduct; additives; silage; environmental impact

INTRODUCTION

Artichoke byproduct is one the most important feed materials for dairy cows in southeastern Spain during winter (Martínez Teruel et al., 1998), and ensilage has been considered the conservation technique with the greatest potential for this byproduct (Megías et al., 1993). However, a low dry matter (DM) content of artichoke must be taken into account to obtain highquality silage. The volume of effluents produced is inversly related to the DM content of the material to be ensiled; Purves and McDonald (1963) recommended DM content >25% so as not to obtain large amounts of effluents. For these authors silage making is inevitably associated with the production of waste and therefore with some degree of unavoidable environmental pollution. The effluents are a strong pollutant of nearby land and water and create an odor problem at the farmstead, the products being transported through the soil-plantanimal system.

The two main parameters relevant to the evaluation of pollutant capacity are the inorganic and organic sediments and microbes found on water surfaces and environmental soil pollution. The total oxygen value is linked to the full organic matter oxidation by a strong chemical oxidant and is expressed by the term chemical oxygen demand (COD). Biochemical oxygen demand (BOD) is defined as the potential for the removal of oxygen from water by aerobic heterotropic bacteria that utilize organic matter for the production of energy and for multiplication. BOD is widely used to detect and assess organic waste contamination levels of water surfaces. If we assume that clean river water has a BOD of \sim 3 mg·L⁻¹, then it is evident that silage effluent is a potentially damaging pollutant. Typical BOD values of effluents are comparatively high, 90000 mg·L⁻¹ (Woolford, 1978); however, little information is available to

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identify the impact on the environment of byproduct silage effluent.

There are three important aspects that have to be considered in the evaluation of the ensilage process of byproduct from canning factories: the nutritive value, the fermentation pattern, and the pollution effect. The prior aims of the present experiment have been to examine the effects of three additives, formic acid (FA), sodium chloride (SC), and cane sugar molasses (M), on silage preservation. A study on seepage was carried out, and the total volume of effluents released was assessed, along with the influence, across time, of artichoke byproduct silage evolution on environmental pollution, with or without the treatment being controlled.

MATERIALS AND METHODS

Materials. Artichoke (*Cynara scolymus* L.) bypoduct is the residue from the industrial processing of artichoke hearts. The artichokes were washed and scalded (at 90 °C for 20 min) and the hearts removed mechanically. The outer bracts and stems were the principal parts of this byproduct. The material was transferred to the laboratory and dried at room temperature for 12 h to eliminate the liquids accumulated during the industrial processing. After this time, the byproducts were ensiled and compressed by hand. The microsilos were sealed, except for an opening at the base, which was sealed after seepage release. Fifty days later, the silos were opened and three samples taken from the center of each ensiled mass. The samples were stored frozen until analyzed for nutritive and fermentative characteristics.

Treatments. The byproduct was mixed thoroughly by hand and subjected to three treatments: (1) byproduct with FA at 20% in doses of 2 mL·kg⁻¹; (2) byproduct with M (50 g·kg⁻¹); (3) byproduct with SC (30 g·kg⁻¹). The effect of using additives was compared with a control without any additive (C). Twelve plastic bags (three replicates per treatment) were filled with byproducts and placed inside a similar number of polyethylene containers. Each silo had a 12.50 L capacity, with a 268.8 cm botton section. The containers were weighed at the beginning of the trial. On each sampling day they were weighed again before the sample was taken out. The gas production was calculated from the difference between the initial weight and the sampling day weight less the effluent weight. **Methods.** The silos were stored at room temperature (21 °C) and opened after 50 days of ensiling. On days 1, 2, 3, 4, 6, 8, 13, and 50 the effluents were removed and the production of effluents was measured.

The methods to determine the different parameters were as follows: three replicates were taken from each silo core and were immediately frozen to -20 °C and later defrosted at 4 °C for 12 h. The initial acidity was determined by taking measurements with a pHmeter from a maceration of the sample in distilled water. Lactic acid was quantified in water extracts of L-(+)- and D-(-)-isomers using L- and D-lactate dehydrogenases (Boehringer Mannhein test kit 1112821, Mannehein, Germany). The amount of ammonia N was measured colorimetrically in water extracts of fresh silage using the Chaney and Marbach (1962) method. The level of volatile fatty acids was determined in water extracts of fresh silage (by capillary gas chromatography) according to the method described by Madrid et al. (1999).

All of the chemicals used were of analytical grade. The determinations of the DM contents were carried out in triplicate using samples of ~300 g dried at 85 °C for 24 h. The dried samples were milled to 0.5 mm. Samples of silage were analyzed for N using the Kjeldahl method, and the amount of crude protein was calculated by multiplying N \times 6.25. Sequential detergent fiber fractions were determined according to the method described by Van Soest et al. (1991). DM digestibility (DMD) and organic matter digestibility (OMD) were calculated according to the method of Vanderhaeghe and Biston (1987). The total mineral content was determined by the incineration of the sample at 500 °C for 3 h in an electric muffle furnace.

Effluents. To the determine the degradation capacity of the effluents and their ambiental impact, other parameters such as the total volume, BOD_5 , COD, pH, conductivity, and total suspended solids (TSS) were determined using the DOE (1989) methods. To assess BOD_5 , the samples were incubated at 20 °C for 5 days, whereas the COD was determined using the closed reflux titrimetric method; the conductivity and pH were determined by means of a conductivity cell and pHmeter, respectively. The TSS was detected by filtration followed by drying at 105 °C for 16 h.

Statistical Analysis. The Tukey test with a significance level of P < 0.05 was employed for the comparison of the means (Steel and Torrie, 1980). For the volume effluents produced fit during the silage process, the Curve Expert 1 program was used.

RESULTS AND DISCUSSION

Characteristic Chemical Composition and Fermentation. The chemical composition was determined 50 days after ensiling was begun. The results with regard to the concentration of organic acids and ammonia N are given in Table 1. The nutritive content of the artichoke was typical of that expected for this byproduct in the region of Murcia, and no mold or surface waste was found in either container.

All silages prepared in this study, including the control, were well fermented. The mean values of lactic acid content for the artichoke with M (105.7 g·kg⁻¹) were higher than those for the artichokes with FA, SC, or C (67.7, 57.7, and 73.7 g·kg⁻¹, respectively). However, this effect was not significantly evident (P > 0.05). Low acetic and butyric acid contents were detected, indicating that the artichoke byproduct was easy to ensile. Nevertheless, the degree of silage fermentation differed considerably between treatments as was also found by Megías et al. (1998) for the same ensiled byproduct, and the acetic acid concentration not did surpass the figure of 19.9 g·kg⁻¹ indicated by Viela (1983) for well-preserved silages.

With regard to pH and ammonia N levels in the silages, all treatments were well preserved with am-

 Table 1. Fermentative Characteristics of Artichoke

 Byproduct after 50 Days of Ensiling^a

	treatment				signif
	FA	М	SC	control	level ^b
pН	3.8 ^{ab}	3.7 ^b	3.6 ^b	4.1 ^a	**
temp inside (°C)	25.5	27.3	26.6	26.3	NS
total gas production (% DM)	9.0	4.6	8.0	8.8	NS
constituents (g∙kg ⁻¹ DM)					
lactic acid	67.7	105.7	57.7	73.7	NS
D-lactic acid	17.8	3.45	18.5	29.9	NS
L-lactic acid	43.2	101.6	37.3	43.6	NS
acetic acid	18.3 ^a	8.8 ^{ab}	5.3^{b}	7.7^{b}	*
propionic acid	2.9^{a}	1.0 ^{ab}	0.8 ^b	1.3^{ab}	*
isobutyric acid	0.5 ^a	0.1 ^{ab}	0.006 ^b	0.1 ^{ab}	*
butyric acid	1.0	0.4	0.4	0.5	NS
N-NH ₄ (mg·100 g ⁻¹ DM)	40.1 ^a	23.5^{ab}	19.1 ^b	27.0 ^{ab}	*
ammoniacal no. (N-NH₄•N ⁻¹ total)	5.1 ^a	3.1 ^{ab}	2.5 ^b	3.3 ^{ab}	*

^{*a*} Means in the same row with different superscript letters are significantly different. ^{*b*} Significance level = (*) P < 0.05, (**) P < 0.01, (***) P < 0.001, (NS) not significant.

 Table 2. Effect of Treatments on Nutritive Composition

 of Artichoke Byproduct after 100 Days of Ensiling^a

	treatment				signif
	FA	М	SC	control	level ^b
DM (g·kg ⁻¹)	137.9	217.9	231.6	162.3	NS
constituents (g·kg ⁻¹ DM)					
crude protein	74.7 ^b	75.0 ^{ab}	76.8 ^a	72.9 ^b	***
crude fat	31.5	27.3	25.4	20.4	NS
WSC	3.6 ^b	5.7^{a}	3.7 ^b	3.7^{b}	**
NDF	553.0 ^a	498.8 ^{ab}	489.1 ^b	548.9^{a}	*
ADF	456.0^{a}	386.9 ^b	395.6 ^b	435.8 ^{ab}	**
cellulose	360.6^{a}	298.8 ^{bc}	260.8 ^c	338.2 ^{ab}	***
hemicellulose	96.9	111.9	93.5	102.7	NS
lignin	37.1	36.4	32.4	30.0	NS
cellular content	447.0 ^b	501.1 ^{ab}	514.8^{a}	451.1 ^b	*
DMD	650.3 ^b	702.5 ^{ab}	740.5^{a}	652.5^{b}	***
OMD	630.0 ^b	691.3 ^{ab}	727.4^{a}	649.2 ^b	**
ash	62.6 ^{ab}	62.6 ^{ab}	82.7 ^a	35.7 ^b	***

^{*a*} Means in the same row with different superscripts letters are significantly different. ^{*b*} Significance level = (*) P < 0.05, (**) P < 0.01, (***) P < 0.001, (NS) not significant.

monia N concentrations $< 100 \text{ g}\cdot\text{kg}^{-1}$ DM (Mayne, 1990). The SC treatment was the most effective as a silage preservative when used with a byproduct containing low DM concentration. The pH of all the treatments after the ensiling period ranged from 3.6 to 4.1 (Table 1). The pH values recorded are typical of lactic fermentation and indicate that the silages were well-fermented. The M and SC treatments decreased (P < 0.01) in proportion to the untreated silage, this result being consistent with that of Megías et al. (1998). When compared directly, both the M and FA treatments significantly decreased (P < 0.01) the concentration of ammonia N compared with the untreated silages, but the effects of FA treatments were greater than those for M, indicating that FA was less effective in improving silage fermentation.

Temperatures inside the silos were low in all cases, averaging 26.4 °C, reflecting a homofermentative process (McDonald et al., 1991). Finally, M was the treatment with the lowest gas production (4.6%) of all the groups, but the differences between batches were not significant.

The effect of the treatments on nutritive composition are presented in Table 2. In general, the addition of SC significantly improved the quality of the chemical composition (P < 0.001). The FA treatment had a lower DM concentration than that of the control or other

Table 3. Effect of Treatments on Effluent Productionduring the 50 First Days and on Environmental Impactof Artichoke Byproduct Silage^a

	treatment				signif
	FA	М	SC	control	level ^b
L·T ⁻¹	52.7 ^{ab}	46.9 ^b	55.2^{ab}	70.1ª	**
% in the first 4 days	40.7 ^b	50.7 ^b	80.7 ^a	40.7 ^b	*
pH (1) ^c	3.9	4.0	3.8	4.1	NS
pH (2) ^c	3.8 ^{ab}	3.7 ^b	3.6 ^b	4.1 ^a	**
BOD ₅ (mg of $O_2 \cdot L^{-1}$) (1)	35156	28125	4882	13281	NS
BOD ₅ (mg of $O_2 \cdot L^1$) (2)	12239	15234	3697.7	7161	NS
COD (mg of $O_2 \cdot L^{-1}$) (1)	57840 ^b	117300 ^a	38807 ^b	82407^{ab}	**
COD (mg of $O_2 \cdot L^{-1}$) (2)	49493	24946	34213	40700	NS
TSS (mg·L ^{-1}) (1)	4.1	3.3	5.5	1.9	NS
TSS (mg·L ^{-1}) (2)	1.3	6	2.1	3.9	NS
cond. ^d ($\mu\Omega^{-1} \cdot cm^{-1}$) (1)	8.7 ^b	8.7 ^b	46.4^{a}	8.3 ^b	**
cond. $(\mu \Omega^{-1} \cdot cm^{-1})$ (2)	8.8 ^b	9.1 ^b	36.5 ^a	7.2 ^b	***

 a Means in the same row with different superscripts letters are significantly different. b Significance level = (*) P < 0.05, (**) P < 0.01, (***) P < 0.001, (NS) not significant. c (1) median value in the 4 first days; (2) median value at day 50. d Conductivity.

treatments. Concentrations of WSC were extremely low, ranging from 3.6 to 5.7 g·kg⁻¹, with the highest recovery being observed in the byproduct treated with molasses and with significant differences between batches.

In the treatment with SC the concentration of the NDF decreased significatly with respect to the control group. Similar results were found for the other sequential detergent fiber fractions. With regard to the SC treatment, the digestibility tended to be higher for this additive than for the other groups. Significant differences were found in DMD and OMD levels between this batch and the control one (P < 0.001, P < 0.01), these results concurring with those of Megías et al. (1998) for artichoke byproduct after 100 days of ensiling.

Effluent Production and Pollutant Capacity during Ensilage. The quantity of effluent produced from silage is related to the grass DM content before ensiling, the use of acid additives, the pretreatment of the crop, the degree of chopping and consolidation at ensiling, the type of silo, and the amount of rolling after ensiling. To ensile artichoke byproduct without causing any environmental impact, it is necessary to improve the fermentation process and to reduce seepage losses. Relatively little research had been conducted on the influence of effluent production on environmental pollution. Hernández Lax et al. (1996) studied the volume of effluents produced by artichoke byproduct ensiled with various additives.

Table 3 summarizes the volume of effluents produced by the silages. Effluents after 50 days of ensiling were significantly (P < 0.01) lower when FA, M, or SC was used than for untreated silage. The result of the control group is consistent with the data found by Zimmer (1964) when turnip leaves were ensiled (79.5 \dot{L} ·T⁻¹) but surpasses that of McDonald et al. (1960) on perennial ryegrass silage. The M treatment had a lower total production (4.7 $L \cdot T^{-1}$) than other treatments. In the context of the present experiment, it appears that the addition of different additives reduces effluent output, even with FA. This fact differs from a number of other studies in which herbage used at ensiling encouraged a rapid release of soluble cell constituents as a result of changes in the lipophilic fraction of plant material. As can be seen in Figure 1, there was a high intensity of fermentation during the first few days. Silages for untreated, FA, and M treatments released most of the effluents during the first 4 days. Gross (1972) discovered



Figure 1. Effects of different treatments on effluent production in artichoke byproduct during 50 days of ensiling.

that 33% of the effluents were produced on the third or fourth days. The SC treatment had a release ratio higher than any other group, with 80.7% of the total volume being produced.

The COD was significantly affected (P < 0.01) depending on the treatment used. The M group showed 117300 mg of $O_2 \cdot L^{-1}$, a much higher content than for FA or SC (57840 and 38807 mg of $O_2 \cdot L^{-1}$, respectively), during the first 4 days of ensiling. Furthermore, the different parameters required to determine the environmental pollution caused by the silage effluents are shown in Table 3. These results are very similar to those found for silage fodder. The BOD₅ is the most common ratio used to evaluate the contamination power of liquid wastes. The control group results are lower (13281 mg of $O_2 \cdot L^{-1}$) than those found by Spillane and O'Shea (1973) for various farm wastes (90000 mg of $O_2 \cdot L^{-1}$) and agree with the results of Monfort (1995), who observed 30000 mg of $O_2 \cdot L^{-1}$ on residues of oil manufacture. Anyway, our effluents have a much higher BOD₅ value than that of domestic sewage, both untreated (500 mg of $O_2 \cdot L^{-1}$) and treated (15-30 mg of $O_2 \cdot L^{-1}$), to be poured into a public channel.

TSS represents the concentration of material in suspension in a liquid effluent. It is an important physical characteristic, and its increase during biological treatments can also give an idea of biomass growth. Mateo Box (1996) proved that the highest TSS limit for the agricultural pollutants of watercourses and soil must be 5 mg·L⁻¹. This point is surpassed only by SC treatment, but no significant differences are found between batches.

The SC treatment has the highest content (46.4 $\mu\Omega^{-1} \cdot \text{cm}^{-1}$) for conductivity, the differences being significant (P < 0.01). The results coincide with those of the Spanish Ministry of Agriculture, which stipulates that river water must hold $< 80 \ \mu\Omega^{-1} \cdot \text{cm}^{-1}$. The conductivity of drinking water in the United States ranges generally from 50 to 1500 $\mu\Omega^{-1} \cdot \text{cm}^{-1}$, although some industrial wastes have conductivities $> 10000 \ \mu\Omega^{-1} \cdot \text{cm}^{-1}$ (SMEWW, 1985).

No significant differences were found between the first 4 days of ensiling and the mean value over the 50 days for any of the parameters in the evaluation of the pollutant capacity.

Conclusions. The data from this experiment demonstrate that artichoke byproduct can be effectively ensiled with sodium chloride, molasses, and formic acid under laboratory conditions. The additives used are forecasted to decrease the total production of effluents; on the other hand, the artichoke byproduct silage effluents are very powerful pollutants, so a container must be used to collecte such sewage. Field research must be performed to determine whether similar results can be achieved in commercial silos and which is the best method of disposal for the effluents.

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