Uses of winery and distillery effluents in agriculture: characterisation of nutrient and hazardous components


Department of Agrochemistry and Environment, Miguel Hernandez University, EPS-Orihuela, Ctra Beniel Km 3.2, 03312-Orihuela (Alicante), Spain
*(E-mail: marian.bustamante@umh.es)

Abstract Twenty-one samples of winery and distillery effluents were collected from different Spanish winery and distillery industries. Electrical conductivity, pH, redox potential, density, organic charge (chemical oxygen demand, biological oxygen demand, total, volatile and suspended solids, oxidisable organic C and polyphenols) and contents of plant nutrients and heavy metals were analysed. The aim of this work was to study the composition of these effluents and to find relationships which would make it possible to use easily determined parameters to estimate their composition. The winery wastewater (WW) and vinasse (V) showed an acidic pH, a high organic load and notable polyphenol, macronutrient, micronutrient and heavy metal contents. Some of these properties are not compatible with agricultural requirements; therefore, conditioning treatment of these liquid wastes is necessary to produce a safe, stable and easily manageable end product. Generally, in both effluent types, significant correlations were found between easily analysable parameters, such as suspended, volatile and total solids, pH, electrical conductivity, density and redox potential, and most of the parameters studied. The linear regression equations obtained permitted an immediate characterisation of the WW and V samples using these parameters.

Keywords Heavy metals; organic matter; plant nutrients; polyphenols; vinasse; winery wastewater

Introduction The disposal of winery and distillery effluents is one of the main environmental problems related to wine and alcohol-producing industries in the Mediterranean countries, of which France, Italy and Spain are the greatest producers (Food and Agriculture Organisation, 2003). Winery wastewater (WW) comes from the water used in the different steps of wine production and contains remains of grape pulp, skin and seeds and different compounds used in filtration, precipitation and cleaning processes. During recent years, the WW production in Spain has been approximately $18 \times 10^6$ m$^3$ year$^{-1}$, which is generated during only a few months of the year (August–October). The Spanish wine industry generates six times more wastewater than France or Italy, mainly due to the low cost of the disposal fee. The distillation of wine, wine lees and grape marc for the production of alcohol and calcium tartrate generates a dark brown effluent called vinasse (V), which contains water used in the distillation process, exhausted wine and wine lees, water-soluble compounds of the grape marc and hydrochloric or sulphuric acid.

To overcome the problems associated with WW and V, different treatment methods have been proposed, in addition to their direct application to agricultural soils as organic fertilisers. The WW treatment methods are physico-chemical and biological. The physico-chemical methods are based on natural evaporation in ponds and intensification of the natural evaporation capacity of the ponds by means of sprinklers and panels (Torrijos and Moletta, 2000). Biological methods are based on anaerobic digestion, with microorganisms in suspension or immobilised (Moletta and Raynal, 1992; Kalyuzhnyi et al., 2000, 2001) and...
aerobic biological treatment (Sorlini et al., 1998). In contrast with the WW treatment methods, there is a greater number of studies on the treatment of V. V is usually stored in evaporation ponds or concentrated by means of four to six evaporation steps (Torrijos and Moletta, 2000). Furthermore, anaerobic digestion (Borja et al., 1993; Lalov et al., 2000), aerobic biological treatment (Beltrán et al., 1999), aerobic fermentation to produce single-cell protein (Selim et al., 1991) and alkaline treatment of mixtures of grape marc, vinasse and wheat straw for ruminant feedstuff (Vaccarino et al., 1993) are possible ways of utilising vinasse. The drawback is that most of the WW and V treatment methods are very expensive and do not provide a comprehensive solution because of the need to dispose of sludge or other by-products derived from the process.

WW contains a high organic load and moderate contents of plant nutrients and it is a low-cost source of water (Torrijos and Moletta, 2000), all of which favour its use as an organic fertiliser. Many authors have studied the composition of winery-sludge, obtained through aerobic depuration of winery effluent, and its effect on plants and soil properties (Levi-Minzi et al., 1997; Sorlini et al., 1998; Masoni et al., 2000; Mariotti et al., 2001). However, not enough data is currently available on WW composition and its agricultural use. V composition varies according to different factors, such as the nature and composition of the wine, wine lees and grape marc, the type of distillation equipment and the distillation and calcium tartrate-producing processes. V shows a significant fertiliser value due to its content of plant nutrients, primarily potassium and calcium, and its high proportion of organic matter (Gloria and Orlando-Filho, 1984). However, this liquid waste also contains phytotoxic, antibacterial and recalcitrant compounds (i.e. phenols and heavy metals) (Beltrán et al., 1999). With regard to the agricultural use of V, Cruz et al. (1991) observed that the addition of this liquid waste during a fifteen-year study maintained soil fertility and increased nitrate concentration in the groundwater.

Therefore, before the WW and V can be properly and safely used, they must be characterised. This work had two aims: firstly, to characterise WW and V from different wineries and distilleries in Spain for agricultural purposes, and, secondly, to find relationships which would make it possible to estimate the composition of these liquid wastes from easily determined parameters.

**Methods**

Twenty-one samples (eight WW and thirteen V) from different wineries and alcohol distilleries were collected throughout Spain. Each sample was divided into two parts, one of which was immediately frozen and kept for oxidisable organic C and soluble polyphenols, while the other was used for the immediate analyses. The electrical conductivity (EC), pH, redox potential (RP), density (d), chemical oxygen demand (COD) and biological oxygen demand (BOD$_5$) were determined according to Standard Methods for the Examination of Water and Wastewater (1998). Total solids (TS), volatile solids (VS) and suspended solids (SS) were assessed gravimetrically, in accordance with standard methods (Standard Methods for the Examination of Water and Wastewater, 1998). Oxidisable organic C (C$_{org}$) and total N (N$_T$) were determined by the Walkley–Black and Kjeldahl methods, respectively, and soluble polyphenols according to Beltrán et al. (1999). 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, micronutrients and heavy metals by atomic absorption spectrophotometry.

Mean values of each parameter were tested for statistically significant differences using one-way analysis of variance (ANOVA). Also, the Pearson correlations between the different parameters studied were calculated and a multiple-regression analysis with
stepwise selection of variables was carried out, in order to find simple equations for estimation of the composition of these wastes from easily determined parameters.

**Results and discussion**

**Characteristics of the liquid residues from the winery and distillery industry**

The results of the analyses carried out on the WW and V samples are summarised in Table 1. No significant differences between these liquid wastes were observed for the pH or \( d \). In both effluents, the pH values were acidic, except in isolated cases, where the WW had a basic pH due to the use of alkaline products in the cleaning processes (Torrijos and Moletta, 2000). However, significant differences were observed in the EC and RP, both parameters being higher in V than in WW.

The values of COD, \( BOD_5 \), different solids (SS, TS and VS), \( C_{org} \) and soluble polyphenols did not differ statistically between the two waste types, mainly due to the high data variability (variation coefficients >50%) (Table 1). Although no significant differences were observed between WW and V for these parameters, their average values were, in general, higher in V. This greater organic charge of V may be due to the origin of this waste.

As regards the macronutrient content, V had higher levels of \( N_T \), possibly due to the presence of exhausted wine lees in this effluent (Table 1). Wine lees, a by-product of the

**Table 1** Main characteristics of winery wastewater (WW) and vinasse (V) samples

<table>
<thead>
<tr>
<th></th>
<th>WW</th>
<th>V</th>
<th></th>
<th>WW</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.5 ± 0.19</td>
<td>4.2 ± 0.52</td>
<td>3.6–11.8</td>
<td>3.3–5.3</td>
<td>18</td>
</tr>
<tr>
<td>EC (S/m)</td>
<td>0.19 ± 0.08</td>
<td>0.52 ± 0.18</td>
<td>0.08–0.31</td>
<td>0.18–1.16</td>
<td>57</td>
</tr>
<tr>
<td>RP (mV)</td>
<td>–56 ± 304</td>
<td>76 ± 153</td>
<td>(–352)–(181)</td>
<td>(–215)–(204)</td>
<td>153</td>
</tr>
<tr>
<td>( d ) (g/cm(^2))</td>
<td>1.01 ± 1.02</td>
<td>1.027 ± 1.002</td>
<td>1.002–1.054</td>
<td>1.002–1.077</td>
<td>2.2</td>
</tr>
<tr>
<td>COD</td>
<td>49,105 ± 738</td>
<td>50,207 ± 4,956</td>
<td>738–296,119</td>
<td>11,815–111,520</td>
<td>56</td>
</tr>
<tr>
<td>BOD(_5) (mg O(_2)/L)</td>
<td>22,418 ± 125</td>
<td>14,542 ± 6,685</td>
<td>125–130,000</td>
<td>6,685–113,615</td>
<td>50</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>5,137 ± 226</td>
<td>12,858 ± 4,956</td>
<td>226–30,300</td>
<td>32–49,767</td>
<td>135</td>
</tr>
<tr>
<td>VS (mg/L)</td>
<td>12,385 ± 661</td>
<td>24,197 ± 4,956</td>
<td>61–54,952</td>
<td>4,767–32,500</td>
<td>85</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>18,336 ± 1,602</td>
<td>38,485 ± 6,685</td>
<td>1,602–79,635</td>
<td>6,685–113,615</td>
<td>81</td>
</tr>
<tr>
<td>Polyphenols (mg/L)</td>
<td>140 ± 29</td>
<td>318 ± 66</td>
<td>29–474</td>
<td>65–766</td>
<td>63</td>
</tr>
<tr>
<td>( C_{org} ) (g/L)</td>
<td>2.16 ± 0.11</td>
<td>4.40 ± 1.09</td>
<td>0.11–9.18</td>
<td>1–9.1</td>
<td>11.12</td>
</tr>
<tr>
<td>( N_T ) (mg/L)</td>
<td>35.4 ± 0.0</td>
<td>104.9 ± 21.3</td>
<td>0.0–142.8</td>
<td>21.3–252.5</td>
<td>74</td>
</tr>
<tr>
<td>P (mg/L)</td>
<td>35.4 ± 176</td>
<td>118.4 ± 1.90</td>
<td>3.3–188.3</td>
<td>190–472.7</td>
<td>126</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>158 ± 107</td>
<td>88 ± 6</td>
<td>7–470</td>
<td>6–570</td>
<td>166</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>270 ± 46</td>
<td>354 ± 313</td>
<td>29–353</td>
<td>313–403</td>
<td>9</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>545 ± 124</td>
<td>2,222 ± 174</td>
<td>187–2,203</td>
<td>174–9,071</td>
<td>143</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>36 ± 67</td>
<td>71 ± 32</td>
<td>16–87</td>
<td>16–87</td>
<td>51</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>12 ± 219</td>
<td>61 ± 4</td>
<td>1–77</td>
<td>4–246</td>
<td>125</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>310 ± 187</td>
<td>1,810 ± 730</td>
<td>&lt;200–1,740</td>
<td>3–3,520</td>
<td>56</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>790 ± 134</td>
<td>1,940 ± 50</td>
<td>&lt;200–3,260</td>
<td>50–8,570</td>
<td>124</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>580 ± 33</td>
<td>1,280 ± 90</td>
<td>90–1,400</td>
<td>90–1,400</td>
<td>50</td>
</tr>
<tr>
<td>Co (mg/L)</td>
<td>170 ± 230</td>
<td>310 ± 90</td>
<td>110–300</td>
<td>90–950</td>
<td>90</td>
</tr>
<tr>
<td>Cr (mg/L)</td>
<td>150 ± 310</td>
<td>70 ± 17</td>
<td>&lt;200–720</td>
<td>10–160</td>
<td>55</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>60 ± 17</td>
<td>980 ± 320</td>
<td>50–80</td>
<td>320–1,740</td>
<td>43</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>1,090 ± 24</td>
<td>300 ± 60</td>
<td>550–1,340</td>
<td>60–810</td>
<td>85</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>120 ± 178</td>
<td>300 ± 60</td>
<td>&lt;200–650</td>
<td>60–810</td>
<td>85</td>
</tr>
</tbody>
</table>

EC: Electrical Conductivity; RP: Redox Potential; \( d \): density; COD: Chemical Oxygen Demand; \( BOD_5 \): Biological Oxygen Demand; SS: Suspended Solids; VS: Volatile Solids; TS: Total Solids; \( C_{org} \): Oxidisable Organic Carbon; \( N_T \): Total Nitrogen; CV: Coefficient of Variation
fermentation and clarification step in the wine-producing process, contains organic matter rich in nitrogen (dead or living yeast and bacteria and grape and additive proteins) (Vogt et al., 1986). The levels of K were also greater in V samples, probably because of the release of potassium from tartaric salts during acidic diffusion of V for the tartaric acid production. The higher Mg contents also noted in V may come from the soluble magnesium salts in the by-products used in the alcohol-producing industries (wine, wine lees and grape marc) (Ribéreau-Gayon et al., 1998). In general, the micronutrient concentrations were statistically higher in the V samples. The Mn concentration in wine ranges from 1 to 3 mg/L and this element is also present in the solid part of the grapes, especially in the seeds. Also, the use of potassium hexacyanoferrate, for Fe elimination in wine, produces Zn precipitation (Ribéreau-Gayon et al., 1998). These facts could explain the greater Mn and Zn contents of V in comparison with WW. The Co, Cr, Cd, Pb and Ni contents were also determined and no significant differences were found in the levels of these elements between the two groups of wastes. In both effluents, the Pb concentration was one of the most prominent among the heavy metals. This might be mainly due to the acidic pH of these liquid wastes, which favours the solubilisation of this element from the metal material of the distillation and wine production equipment. Mean values in rows followed by the same letter do not differ significantly ($P < 0.05$) between the groups of residues.

Both groups of residues studied showed lower pH average values and higher $N_T$, Na and, in general, micronutrients and heavy metals average contents than the limits established by Westcot and Ayers (1990) for irrigation water. However, the direct application of WW to agricultural soils might not increase the soil salinity, since its average EC value was well below the established limits for irrigation water (Westcot and Ayers, 1990). On the other hand, the presence of polyphenols in WW and V considerably increases the biochemical and chemical oxygen demands, with detrimental effects on the micro-organisms and plants of the discharge zones; thus, a conditioning treatment of these wastes is necessary.

Relationships between the main analytical parameters of WW and V samples
The variation coefficients of the parameters studied (Table 1) reveal a high degree of randomness in most of these parameters, which means that these wastes should be characterised fully before being used for agricultural purposes. Since a full characterisation would be very time-consuming, it would be useful to establish equations which would make it possible to estimate most of the parameters from others that are more easily determined.

The study of the interrelationships of WW characteristics indicated that easily determined parameters, such as SS, VS, TS and $d$, were significantly correlated ($P < 0.01$ (*) and 0.001 (**)) with most of the other parameters (Pearson correlation coefficients ranged from 0.841 to 1.000), possibly because most of the parameters studied (COD, BOD$_5$, polyphenol and $C_{org}$ contents, etc.) were related to the organic matter of this effluent. Also, the pH showed significant correlations with Na and K (Pearson correlation coefficients $= 0.732^*$ and $-0.869^{**}$, respectively), which could be related to the alkaline hydrolysis of Na salts from wine additives and the low solubility of potassium hydrogen tartrate at high pH values (Ribéreau-Gayon et al., 1998; Escudier et al., 2000). On the other hand, RP was only correlated with Pb (Pearson correlation coefficient $= 0.742^*$).

In the case of V, fewer parameters were interrelated, in comparison with the WW. However, the SS, VS, TS and $d$ once again proved to be the best parameters for the estimation of the V composition (Pearson correlation coefficients ranged from 0.669 to 0.994, significant at $P < 0.01$ and 0.001). In addition, the pH showed significant correlations with Ca, Co, Cd, Pb and Ni (Pearson correlation coefficients $= 0.833^{***}$, $0.831^{***}$, $0.825^{***}$, $0.871^{***}$ and $0.831^{***}$, respectively), whereas the EC was correlated with Mg (Pearson
### Table 3

Parameters of the multiple linear regression (stepwise method) and coefficients of determination (100x adjusted $R^2$) corresponding to the equations fitted between total solids (TS), suspended solids (SS), volatile solids (VS), density ($d$), redox potential (RP), pH and electrical conductivity (EC) and chemical oxygen demand (COD), biological oxygen demand (BOD$_5$) and contents of oxidisable organic C ($C_{\text{org}}$), macro and micronutrients, heavy metals and polyphenols, for the V samples

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>PVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg O$_2$/L)</td>
<td>$5.44^{***}$ VS (mg/L) – $2769^{NS}$</td>
<td>99.9***</td>
</tr>
<tr>
<td>BOD$_5$ (mg O$_2$/L)</td>
<td>$5.45^{**<em>}$ VS (mg/L) – $3522^{</em>}$ EC (S/m)+$4052^{NS}$</td>
<td>100*</td>
</tr>
<tr>
<td>Polyphenols (mg/L)</td>
<td>$2.37^{***}$ VS (mg/L) – $389^{NS}$</td>
<td>99.9***</td>
</tr>
<tr>
<td>C$_{\text{org}}$ (g/L)</td>
<td>$0.008^{***}$ VS (mg/L)+$42.68^{NS}$</td>
<td>97.1***</td>
</tr>
<tr>
<td>P (mg/L)</td>
<td>$0.0075^{<strong>}$ VS (mg/L) – $0.046^{</strong>}$ TS (mg/L)+$66.15^{***}$</td>
<td>100*</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>$1.610^{-4^{***}}$ VS (mg/L)+$0.116^{NS}$</td>
<td>99.8***</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>$0.024^{**<em>}$ TS (mg/L)+$236^{</em>}$</td>
<td>98.5***</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>$0.019^{*<strong>}$ VS (mg/L) – $1249^{</strong>}$</td>
<td>94.5**</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>$0.008^{<em><strong>}$ VS (mg/L) – $0.046^{</strong>}$ TS (mg/L)+$66.15^{</em>**}$</td>
<td>99.8***</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>$0.022^{***}$ VS (mg/L)+$32.30^{NS}$</td>
<td>99.3***</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>$0.029^{<em><strong>}$ VS (mg/L) – $0.046^{</strong>}$ TS (mg/L)+$66.15^{</em>**}$</td>
<td>99.8***</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>$0.025^{**<em>}$ TS (mg/L)+$236^{</em>}$</td>
<td>98.5***</td>
</tr>
<tr>
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<td>$0.019^{*<strong>}$ VS (mg/L) – $1249^{</strong>}$</td>
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<td>$0.008^{<em><strong>}$ VS (mg/L) – $0.046^{</strong>}$ TS (mg/L)+$66.15^{</em>**}$</td>
<td>99.8***</td>
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<td>Mn (mg/L)</td>
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<td>Zn (mg/L)</td>
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<td>Cu (mg/L)</td>
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*: Significant at $P < 0.05$, $0.01$, $0.001$, respectively. NS: Not significant
PVE: Percentage of variance explained
correlation coefficient = 0.777**) and the RP with Na, Ca and Ni (Pearson correlation coefficients = −0.714**, −0.622* and −0.610*, respectively). These correlations could be due to the interrelationships between pH, EC and RP and the solubility of these elements.

Tables 2 and 3 show the linear regression equations, for the WW and V samples, respectively, obtained between the easily analysable parameters (SS, VS, TS, d, EC and PR) and most of the other parameters studied, which are more difficult to analyse (COD, BOD5, polyphenols, C\textsubscript{org}, macronutrients, micronutrients and heavy metals). The percentage of variance explained (PVE) by each model is also shown in these tables. The high PVE values in both groups of equations, between 82 and 100%, indicate a high level of correlation. In the case of WWs, a higher number of parameters could be calculated with the equations using the SS, VS, TS, d, pH and RP. Furthermore, the PVE for these equations was higher than for those determined for Vs. In both wastes, it was found that the constant and the intercept of the equations for most of the parameters were statistically significant; therefore, most of the parameters studied can be estimated using the complete equation.

**Conclusions**

Both groups of residues were characterised by an acidic pH, a high organic charge and notable polyphenol, Nr, Na and, in general, micronutrient and heavy metal contents, which do not favour their direct application to agricultural soils. Therefore, conditioning treatments prior to the use of the WW and V are necessary.

These effluents should be characterised completely before their use and treatment, due to the great variation found in most of the parameters determined in both the WW and V samples. In both wastes, SS, VS, TS, d, pH, EC and RP can be taken as easy-to-determine reference parameters for estimating the parameters related to possible environmental risks, which are much more difficult to analyse chemically.

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**References**


