Combining UASB technology and advanced oxidation processes (AOPs) to treat food processing wastewaters

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Abstract

UASB treatment of fruit cannery and winery effluents was shown to be feasible. However, the treated effluents still have residual COD levels well above the legal limit of 75 mg.l⁻¹ for direct discharge to a water system and a form of post-treatment is necessary to reduce the COD further. Ozone and ozone/hydrogen peroxide were used in combination with a granular activated carbon contacting column to assess the effectiveness as a post-treatment option for the UASB treated fruit cannery and winery effluent. Colour reduction in the effluents ranged from 66 to 90% and COD reductions of 27–55% were achieved. The combination of ozone and hydrogen peroxide gave better results than ozonation alone. Significant progress was thus made in achieving the legal limit of 75 mg.l⁻¹.

Keywords

Cannery effluent; granular activated carbon; hydrogen peroxide; ozone; post-treatment; UASB; winery effluent

Introduction

Due to the nature of the fruit and vegetable canning process, large volumes of water are used in product transportation, washing and rinsing, blanching, retorting and cooling operations (Water Research Commission, 1987a; Wayman, 1996). The wine industry is no different, producing large volumes of wastewater throughout the year. Most of the water originates from cellar cooling and floor and equipment washdown (Ronquest, 1999). These industries are thus faced with firstly, maintaining a profitable level of production while reducing the intake of fresh, potable water, and secondly, disposing of the large volumes of effluent in an environmentally responsible manner.

Treatment of these effluents (seasonal fruit cannery and winery) by upflow anaerobic sludge blanket (UASB) reactors has recently been shown to be a feasible option. COD reductions of up to 93% at organic loading rates (OLR) of 10.95 kgCOD.m⁻³.d⁻¹ and hydraulic retention times (HRT) of <12 h (Tnovec and Britz, 1998) were achieved treating a fruit canning wastewater. Similarly, COD reductions of 93% at an OLR of 11.05 kgCOD.m⁻³.d⁻¹ and a HRT of 14 h were achieved treating a winery wastewater (Ronquest, 1999). In many instances the COD level of the final effluent is still well above the South African legal limit permitted for wastewaters (75 mg.l⁻¹) to be discharged to a water system (Water Research Commission, 1987b) and a further post-treatment is thus necessary.

The use of advanced advanced oxidation processes (AOPs) in the treatment of wastewaters has recently become popular (Hunt and Mariñas, 1997; Camel and Bermond, 1998). AOPs have been defined as processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification. The most common processes are O₃/H₂O₂, O₃/UV and H₂O₂/UV. The use of these AOPs is thus an attempt to produce the maximum amount of these hydroxyl radicals (Gottschalk et al., 2000). The hydroxyl radical has a high oxidation potential (2.8 eV) and attacks organic molecules by either abstracting a hydrogen atom or by adding to double bonds. Organic molecules are thus mineralized to non-toxic forms such as carbon dioxide or water (Mourand et al., 1995; Gulyas et al., 1995; Beltrán et...
al., 1999). Some organic compounds react rapidly with ozone leading to destruction, while others are only partially oxidized. Partially oxidized molecules become more polar, producing more complexed insoluble materials which are then easily removed/absorbed by activated carbon filters (Gulyas et al., 1995). Granular activated carbon (GAC) is thus used effectively in removing taste and odour compounds, colour, organics, excess chlorine, pesticides and toxic and mutagenic substances, due to the large adsorption area (500–600 m²·g⁻¹) available (Bitton, 1994).

The COD contents of several food processing wastewaters have been successfully degraded using ozone, H₂O₂ and/or UV, including fruit cannery, distillery, poultry and tomato processing wastewaters (Chang and Sheldon, 1989; Beltrán et al., 1997; Sigge et al., 2001). Lowering of the polyphenol contents of table olive debittering wastewaters (Beltrán et al., 1999) and decolorization of yeast-production industry wastewaters has also been achieved (Filipovic-Kovacevic and Sipos, 1995).

The aim of this study was to investigate the possibilities of using combinations of UASB technology, ozonation, granular activated carbon and hydrogen peroxide to treat cannery and winery wastewaters.

**Materials and methods**

**Effluents**

A fruit cannery effluent with an average COD of 7,500 mg·l⁻¹ and pH of ca. 5.0 was collected from a nearby fruit cannery during the apricot canning season. After sedimentation, to separate the excess solid material, the pH of the effluent was adjusted to 7.5 before use as substrate for anaerobic treatment.

A winery effluent with an average COD of 3,700 mg·l⁻¹ and pH of ca. 4.8 was collected from a local winery. Solid material was removed by sedimentation and the pH of the effluent was then adjusted to 7.5 before use as substrate for anaerobic treatment.

**Anaerobic treatment**

A 2.3 l laboratory-scale upflow anaerobic sludge blanket (UASB) bioreactor was used (Trnovec and Britz, 1998) and operated at 35°C (Meyer et al., 1985). The volume of the biogas was determined using a manometric unit equipped with an electronically controlled counter and a gas-tight valve and the volumes corrected to standard temperature and pressure. The substrate was fed semi-continuously to the bioreactor by means of a peristaltic pump (Watson-Marlow 302S) controlled by an electronic timer. The bioreactor was run at a HRT of 24 h. The pH, COD, alkalinity, orthophosphate phosphorous, total solids of the bioreactor effluent were monitored (Standard Methods, 1992).

**Oxidation**

Ozonation of the UASB treated fruit cannery and winery effluent was done in a continuous mode, bubble/GAC contacting setup. This consisted of a glass bubbling column connected to a GAC column. Ozone was bubbled upwards through the glass column, while the effluent was re-circulated from the bubbling column through a GAC contacting column. The bubbling column (l = 90 cm; ∅ = 6 cm) had a sintered glass disc at one end for bubble generation. The GAC contacting column consisted of a closed stainless steel cartridge (l = 20 cm; ∅ = 6.5 cm) filled with granular activated carbon. An ozone generator (Oz Purification, Ifafi) producing 9.0 g ·h⁻¹ O₃ at a flowrate of 4 l·h⁻¹ was used for the ozonation trials. The effect of hydrogen peroxide (H₂O₂) addition to the oxidation treatments was also investigated by adding 1% H₂O₂ to the bioreactor effluent before ozonation. The different continuous mode treatment combinations studied are summarized in Table 1.
Analytical methods
The ozone production was measured using an iodiometric titration (Standard Methods, 1992) and residual ozone concentrations in the effluent were determined using the DPD Method (Hach Co., Loveland, CO). COD was determined colorimetrically using a DR2000 spectrophotometer (Hach Co., Loveland, CO) and standardised procedures (Standard Methods, 1992). Colour removal in the effluent was determined by monitoring the absorbance of the effluent at 288 nm using a Spectronic® 20 Genesys™ spectrophotometer (Spectronic Instruments, USA).

Results and discussion
Anaerobic digestion
During the anaerobic treatment of the cannery effluent the COD was lowered by 90–93%. The bioreactor effluent had a pH of 7.0–7.2 and a COD concentration of 525–750 mg.l⁻¹. The effluent from the bioreactor treating the winery effluent had a pH of 7.2–7.4 and a COD concentration of 148–370 mg.l⁻¹, constituting COD reductions of 90–96%. These bioreactor effluents were used in the oxidation studies.

Oxidation
Oxidation treatments resulted in significant colour reductions, as can be seen from Table 2. Increases in the treatment time led to increases in colour reduction of 66% after 5 min to 90% after 30 min. The addition of 1% H₂O₂ (v/v) to the 5 and 15 min oxidation treatments led to slight increases in colour reduction (from 66 to 70% and 87 to 90%, respectively) for the effluent from the bioreactor treating cannery wastewater. The same tendency was found for the effluent from the bioreactor treating a winery wastewater. Increases in ozonation time increased colour reduction from 68% (5 min O₃) to 87% (30 min O₃), with increases from 68 to 71% and 83 to 88% when adding 1% H₂O₂ (v/v) to the 5 and 15 min oxidation treatments, respectively. These results compare favourably with previous studies on the reduction of UASB bioreactor effluent colour with O₃ and H₂O₂ (Sigge et al., 2001). The colour reductions achieved in this study were, however, somewhat higher. This could possibly be due to the inclusion of a GAC contacting column in the continuous mode oxidation used in this study. Beltrán et al. (1997, 1999) also found that H₂O₂ alone was not an effective oxidizing agent in the treatment of tomato processing wastewaters and distillery wastewaters.

The oxidation treatments were also effective in reducing the COD of the effluents. Increases in the ozonation time led to increases in COD removals from 27 and 30% after 5 min to 53 and 55% after 30 min for effluents from bioreactors treating cannery and winery wastewaters, respectively (Figure 1). Similar increases in COD reduction with increased reaction time were also found when treating UASB treated alkaline cannery effluent (Sigge et al., 2001), debittering table olive and (Beltrán et al., 1999), yeast-production industry
wastewaters (Filipovic-Kovacevic and Sipos, 1995), chlorinated aromatics (Schmitt and Hempel, 1993), tomato and distillery wastewaters (Beltrán et al., 1997). It is also clear from the data in Figure 1 that the increases in COD reduction over time are not linear. Initially the rate of COD degradation is rapid, but the rate decreases with time. This can probably be ascribed to the fact that some organic compounds are more susceptible to oxidation than others, while some are only partially oxidized (Camel and Bermond, 1998). This indicates that the UASB effluents contain a considerable amount of difficult to oxidize compounds that require a stronger oxidizing system.

The slightly higher reductions in the bioreactor effluent COD achieved in this study, using ozone in the continuous mode compared to the batch method (Sigge et al., 2001) are probably the result of the GAC contacting column. Certain molecules are only partially oxidized by ozone, forming lower molecular weight compounds, which are better adsorbed on the GAC column (Camel and Bermond, 1998), thus lowering the effluent COD.

![Figure 1 COD removal during the different treatment conditions used in the post-UASB treatment of alkaline fruit cannery effluent](image)

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**Table 2** The effect of oxidation treatments on the colour of effluents from UASB bioreactors treating fruit cannery and winery wastewaters

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Absorbance (288 nm)</th>
<th>Colour reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioreactor effluent (cannery)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min O₃</td>
<td>0.516</td>
<td>66</td>
</tr>
<tr>
<td>10 min O₃</td>
<td>0.258</td>
<td>83</td>
</tr>
<tr>
<td>15 min O₃</td>
<td>0.196</td>
<td>87</td>
</tr>
<tr>
<td>30 min O₃</td>
<td>0.153</td>
<td>90</td>
</tr>
<tr>
<td>1% H₂O₂ (v/v) + 5 min O₃</td>
<td>0.457</td>
<td>70</td>
</tr>
<tr>
<td>1% H₂O₂ (v/v) + 15 min O₃</td>
<td>0.152</td>
<td>90</td>
</tr>
<tr>
<td>Bioreactor effluent (winery)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min O₃</td>
<td>0.166</td>
<td>68</td>
</tr>
<tr>
<td>10 min O₃</td>
<td>0.104</td>
<td>80</td>
</tr>
<tr>
<td>15 min O₃</td>
<td>0.088</td>
<td>83</td>
</tr>
<tr>
<td>30 min O₃</td>
<td>0.068</td>
<td>87</td>
</tr>
<tr>
<td>1% H₂O₂ (v/v) + 5 min O₃</td>
<td>0.151</td>
<td>71</td>
</tr>
<tr>
<td>1% H₂O₂ (v/v) + 15 min O₃</td>
<td>0.062</td>
<td>88</td>
</tr>
</tbody>
</table>
Addition of 1% H$_2$O$_2$ (v/v) to oxidation treatments resulted in slight increases in COD reductions over treatments only being ozonated (Figure 1). With the 1% H$_2$O$_2$ (v/v) addition to the 5 min ozonation, the COD reduction increased from 32 to 34%, while an increase from 48 to 50% was achieved with the 15 min ozonation. The increase in COD reduction with increased ozonation time and addition of H$_2$O$_2$ were expected as both lead to formation of more hydroxyl radicals, and thus create a stronger oxidizing capability (Beltrán et al., 1997; Hughes, 1992). The same tendency was found by Sigge et al. (2001) when ozonating an UASB treated fruit cannery effluent. Slightly higher COD reductions were, however, achieved in this study using the continuous mode of oxidation and 1% H$_2$O$_2$ (v/v) additions (i.e. 48 and 50% compared to 45% for a 15 min O$_3$ treatment). Hydrogen peroxide on its own is expected to be less effective due to its lower oxidation potential in comparison to ozone and the hydroxyl radical (Hughes, 1992; Mourand et al., 1995).

Conclusions
Advanced oxidation processes and the use of GAC can be successfully used in combination to lower the COD of UASB treated cannery and winery effluents. The use of a continuous mode of oxidation (inclusion of a GAC contacting column through which the effluent is recirculated during ozonation) resulted in an improvement in colour and COD reduction. These increases can probably be ascribed to the GAC contacting column, where adsorption of organic molecules is taking place. A longer contact time with the GAC would, however, seem to be beneficial in lowering the COD even further. This is deduced from the fact that batch ozonated effluents filtered by GAC with long retention times (8–12 h) resulted in significantly higher COD reductions. In the continuous mode oxidation process the total GAC surface area is also considerably smaller than the GAC filter used in the batch method. Ozone, hydrogen peroxide and GAC can nevertheless be successfully applied in combination treatment processes to lower the COD of UASB treated fruit cannery and winery effluents.

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References


Standard Methods for the Examination of Water and Wastewater (1992). 18th edn, American Public Health Association APHA, American Water Works Association (AWWA) and Water Environment Federation (WEF), Washington DC, USA.


