The efficacy of ozone as a pre- and post-treatment option for UASB-treated food processing wastewaters

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Abstract The efficiency of ozone as a pre- and post-treatment to UASB treatment was investigated, followed by a study into UASB reactor performance with ozonated wastewater as substrate. Combinations of pre- and/or post-ozonation with UASB treatment gave better results than ozonation or UASB alone and COD reductions of 53.0–98.9% were achieved for treatment of canning and winery wastewaters. A UASB reactor was fed with pre-ozonated cannery wastewater for over 70 d. COD removal improved from between 58.8 and 64.4% to between 85.3 and 91.8% after pre-ozonated substrate feed commenced. Subsequent increases in organic loading rate (OLR) from 2.4 to 3.4 kgCOD m\(^{-2}\)·d\(^{-1}\) did not affect reactor performance. By including a final post-ozonation treatment to this UASB effluent a total COD reduction of 99.2% was achieved.

Keywords Canning; ozone; pre-treatment; post-treatment; UASB; wastewater; winery

Introduction

The fruit canning and winery industries are major water users and generate large volumes of polluted wastewater annually (Water Research Commission, 1987a and b). Most of the water-intake is used for product transportation, washing, rinsing, blanching, retorting, cooling and floor and equipment washdowns (Ronquest and Britz, 1999). These industries are faced with increasing legislative pressure to reduce the impact their wastewaters have on the environment, especially in reaching the legal discharge (75 mg L\(^{-1}\)) limit for wastewater (Republic of South Africa, 1999).

Anaerobic digestion has been shown to be feasible for treating food processing wastewaters. These wastewaters usually have a high organic content, have little or no toxic material present and thus, due to their nature and strength, are ideal substrates for anaerobic digestion (Lettinga et al., 1997). The use of the upflow anaerobic sludge blanket (UASB) design to treat seasonal fruit cannery and winery wastewaters has been shown to be a feasible option (Trnovec and Britz, 1998; Ronquest and Britz, 1999; Sigge et al., 2002).

The use of ozone in the treatment of wastewaters has been shown to be effective in reducing COD, removing colour and making compounds more biodegradable (Gottschalk et al., 2000). The success of ozone is dependant on the formation of the hydroxyl radical, a reactive intermediate, which has a higher oxidation potential (2.8 eV) than ozone (2.07 eV). During oxidation, the organic molecules are mineralised to non-toxic forms such as carbon dioxide or water (Gulyas et al., 1995; Beltrán et al., 1999). Some organic compounds react more slowly with ozone, sometimes resulting in the formation of organic solutes which are more susceptible to subsequent biological oxidation (Gulyas et al., 1995; Gottschalk et al., 2000). The COD contents of various food processing wastewaters have been successfully treated using post-ozonation/oxidation treatments, including fruit cannery, distillery, poultry processing, yeast-production and table olive
debittering wastewaters (Chang and Sheldon, 1989; Filipović-Kovačević and Sipos, 1995; Beltrán et al., 1997, 1999, 2001). However, very little research on the use of ozone as a pre-treatment to anaerobic digestion can be found in the literature. Ozone in combination with other oxidants was shown to be effective as a pre-treatment to anaerobic digestion of winery, vinaise and olive oil mill wastewaters (Andreozzi et al., 1998; Benitez et al., 1999; Martín et al., 2002). Wastewater COD reduction and the efficiency of the subsequent anaerobic digestion were improved by pre-ozonation. The effects of pre-ozonation, however, need to be investigated in wastewaters of varying composition.

The aim of this study was firstly, to investigate the short-term efficiency of ozonation as a pre- and post-treatment to UASBs treating fruit cannery and winery wastewaters and, secondly, to investigate the long-term effects of pre-ozonation on the performance of a UASB reactor treating a pre-ozonated fruit cannery wastewater.

**Materials and methods**

**Wastewaters**

A fruit cannery wastewater with an average COD of 7,500 mg L$^{-1}$ (7,430–7,612 mg L$^{-1}$) and pH of ca. 5.0 was collected from a nearby fruit cannery (Rhodes Fruit Farms, Groot Drakenstein) during the apricot canning season. Solid material was removed by sedimentation and the pH of the wastewater was adjusted to 7.5 before use as substrate for anaerobic treatment.

A winery wastewater with an average COD of 3,700 mg L$^{-1}$ (3,647–3,799 mg L$^{-1}$) and pH of ca. 4.8 was collected from a local winery (Fredericksburg, Simondium). Solid material was removed by sedimentation and the pH of the wastewater was then adjusted to 7.5 before use as substrate for anaerobic treatment.

For the investigation of the long-term effects of pre-ozonation on the performance of a UASB reactor, a fruit cannery wastewater with an average COD of 6,500 mg L$^{-1}$ (6,360–6,725 mg L$^{-1}$) and pH of ca. 6.0 was collected from the cannery (Rhodes Fruit Farms, Groot Drakenstein) during the peach canning season. Solid material was removed by sedimentation. Batches of the peach canning wastewater were also frozen for later use. The frozen wastewater was thawed and then diluted to the required COD and the pH adjusted to 7.5 before use as substrate for anaerobic treatment.

Ozone pre-treated peach canning wastewater was prepared in a continuous mode, bubble/granular activated carbon (GAC) contacting setup (Sigge et al., 2002). An ozonation time of 10 min was used. After ozonation the pre-treated wastewater was diluted to the required COD and the pH adjusted to 7.5 before use as substrate in the anaerobic treatment.

**Anaerobic treatment**

A 2.3 L laboratory-scale UASB reactor (Trnovec and Britz, 1998) was operated at 35°C (Meyer et al., 1985). The fruit canning and winery substrates were fed semi-continuously to the reactors by means of peristaltic pumps (Watson-Marlow 302S) controlled by electronic timers. The reactors were run at a HRT of 24 h. The pH, COD, alkalinity, orthophosphate phosphorous and total solids of the reactor effluents were monitored (Standard Methods, 1992).

Once post-treatment trials had been completed the UASB reactors were fed with ozone pre-treated fruit cannery and winery wastewater substrates for a period of 14 days. The resulting UASB reactor effluents (of the last 4 days) were again treated with ozone and the pre- and post-UASB treatment samples (quadruple samples) were considered. The different short-term pre- and post-treatment combinations studied are summarised in Table 1.
The 2.3 L laboratory-scale UASB reactor used earlier to treat an apricot canning wastewater was used for the investigation into the long-term effects of pre-ozonation on the performance of a UASB reactor. In order to monitor any possible improvement in efficiency due to pre-ozonation, a quarter of the granules were removed from the UASB reactor, thus lowering the initial reactor efficiency. The reactor was run at an HRT of 24 h. The initial substrate concentration was ca. 3,500 mg L\(^{-1}\), but was later reduced to ca. 2,400 mg L\(^{-1}\). The pH, COD, alkalinity, orthophosphate phosphorous and total solids of the reactor effluent were monitored (Standard Methods, 1992). The concentration of short chain volatile fatty acids (SCVFA) in the reactor effluent was determined by gas chromatography.

Ozonation
Ozonation of wastewaters and UASB effluents was done in a continuous mode bubble/GAC contacting setup, as described previously (Sigge et al., 2002). An ozone generator (Oz Purification, Ifafi) producing 9.0 g h\(^{-1}\) O\(_3\) at a flowrate of 4 L h\(^{-1}\) was used for the ozonation trials. The different short-term pre- and post-treatment combinations studied are summarised in Table 1.

Analytical methods
The ozone production was measured using an iodiometric titration (Standard Methods, 1992). The COD was determined colorimetrically using a DR2000 spectrophotometer (Hach Co. Loveland, CO) and standardised procedures (Standard Methods, 1992). All analyses were done in triplicate.

Short chain volatile fatty acids
SCVFAs were determined using a Varian 3700 gas chromatograph (GC) equipped with a flame ionisation detector and a 30 m bonded phase Nukol (Supelco Inc., Belafonte, PA) capillary column (0.53 mm diameter and 0.50 µm film thickness). The column temperature was initially held at 105 °C for 2 min, increased at 10 °C min\(^{-1}\) to 190 °C and held for 10 min. The injector temperature was set at 150 °C, while the detector was set at 300 °C. Nitrogen was used as the carrier gas at a flowrate of 6.1 mL min\(^{-1}\). All analyses were done in triplicate.

Biogas composition
The biogas composition was determined on a Varian 3300 GC equipped with a thermal conductivity detector and a 2.0 m × 3.0 mm i.d. column packed with Haysep Q (Supelco Inc., Bellefonte, PA), 80/100 mesh. The oven temperature was set at 55 °C and helium was used as carrier gas at a flow rate of 30 mL min\(^{-1}\).

<table>
<thead>
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<th>Treatment</th>
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<tr>
<td>1</td>
<td>10 min ozonation of raw wastewater</td>
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<tr>
<td>2</td>
<td>UASB treatment of raw wastewater</td>
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<td>3</td>
<td>UASB treatment of raw wastewater + 10 min ozonation (post-treatment)</td>
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<td>4</td>
<td>10 min ozonation of raw wastewater + UASB treatment (pre-treatment)</td>
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<td>5</td>
<td>10 min ozonation of raw wastewater + UASB treatment + 10 min ozonation (pre- and post-treatment)</td>
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Table 1 Short-term pre- and post-treatment combinations of the fruit cannery and winery wastewaters
Results and discussion
Short-term efficiency of ozone as a pre- and/or post-treatment to UASB anaerobic digestion

During the anaerobic treatment of the cannery wastewater by UASB the COD was lowered by 86.9–89.1%. The reactor effluent had a pH of 7.0–7.2 and a COD concentration of 817.5–982.5 mg L\(^{-1}\). The effluent from the reactor treating the winery wastewater had a pH of 7.2–7.4 and a COD concentration of 303.4–399.6 mg L\(^{-1}\), constituting COD reductions of 89.2–91.8%.

COD reductions for the various treatment combinations are summarised in Figure 1. Ozonation of the raw cannery and winery wastewaters for 10 min brought about reductions of 53.0 and 61.7% in the total COD content, respectively. A UASB treatment of the cannery and winery wastewaters resulted in total COD reductions of 88.0 and 90.5%, respectively. Post-UASB ozonation (UASB + 0 min) of the reactor effluents achieved total COD reductions of 92.0 and 93.7%, respectively. Similar reductions in total COD (ca. 95%) were previously reported (Sigge et al., 2002) for post-ozonation treatment of effluent from UASBs treating cannery and winery wastewaters. Pre-treatment of the wastewaters with ozone prior to UASB treatment (10 min + UASB), resulted in the total COD being reduced to 93.5 and 97.5% (Figure 1). A further 10 min ozonation of these UASB effluents led to a total COD reduction of 95.0 and 98.9% being achieved (pre- and post-ozonation), respectively for cannery and winery wastewaters. Final COD values for the pre- and post-treated wastewaters were on average 375 mg L\(^{-1}\) for the cannery wastewater and 40.7 mg L\(^{-1}\) for the winery wastewater. The latter COD value falls well below the South African legal limit of 75 mg L\(^{-1}\) for discharge to a natural water system (Water Research Commission, 1987b). The COD reductions, for ozone treatment alone (53.0–61.7%) compare favourably with previous results achieved by other authors. Benitez et al. (1999) achieved 20–30% COD reduction by ozonating winery wastes, while COD reductions of 41.4%, 65% and 47–62% were reported for ozonation of wine-distillery, yeast production and poultry processing wastewaters, respectively (Chang and Sheldon, 1989; Filipović-Kovačević and Sipos, 1995; Beltrán et al., 2001).

**Figure 1** COD removal during the different treatment combinations used in the pre- and post-treatment of fruit cannery and winery wastewaters.
Long-term effect of an ozone pre-treatment on the performance of a UASB reactor treating a fruit cannyery wastewater

The UASB reactor efficiency is represented in Figure 2. During the initial substrate acclimatisation period (days 1–40) the substrate COD was ca. 3,500 mg L$^{-1}$. During this period the COD removal efficiency did not stabilise and the SCVFA concentration varied dramatically (Figure 2), leading to an unstable reactor pH. It was decided to lower the substrate COD to ca. 2,400 mg L$^{-1}$, which resulted in a more stable operation of the UASB (days 41–72). COD removal stabilised at between 58.8 and 64.4%, which is significantly lower than expected for an optimised UASB, but probably due to the removal of a quarter of the granular biomass resulting in a reduced capacity. The SCVFA content of the reactor effluent stabilised, and averaged 327 mg L$^{-1}$ (day 41–72). The biogas produced by the reactor on day 72 contained 28.1% methane.

Pre-ozonated substrate replaced the normal substrate on day 73 (Figure 2 – vertical line B). Pre-ozonation of the peach cannyery wastewater had resulted in a COD reduction of ca. 55%, lowering the raw wastewater COD to ca. 3,000 mg L$^{-1}$. Before feeding the pre-ozonated wastewater to the UASB, the COD was diluted to ca. 2,400 mg L$^{-1}$ for use as reactor substrate (OLR $= 2.4$ kg COD m$^{-3}$ d$^{-1}$). The substrate COD was kept constant at ca. 2,400 mg L$^{-1}$ until day 122 (Figure 2 – vertical line C), after which the dilution was gradually reduced. By day 138 the undiluted, pre-ozonated peach canning wastewater, with a COD of 3,400 mg L$^{-1}$, was being fed as substrate.

The COD removal of the reactor stabilised at ca. 61% by day 73. A significant improvement in COD removal was observed from day 76 onwards with the pre-ozonated substrate (Figure 2). COD removal reached 79.5% by day 81 and increased to 85.3–90.1% by day 87. The COD removal efficiency remained between 85.3 and 91.8% until the end of the trial (day 144). Together with the improvement in COD removal efficiency during this period (days 76–122), a decrease in SCVFA content of the reactor effluent was also observed (Figure 2). The SCVFA content during this phase averaged 228 mg L$^{-1}$. During this time (days 76–122) the methane percentage in the biogas gradually increased from 28.1% to 36.5%. The gradual increase in substrate COD from day 122 did not negatively influence the COD removal efficiency, which remained between 85.3 and 91.8%, while the OLR increased to 3.4 kg COD m$^{-3}$ d$^{-1}$. A slight increase in the reactor effluent SCVFA content was, however, observed. Methane production increased slightly from 36.5 to 38.3% during this final stage (days 122–144). The

![Figure 2](https://iwaponline.com/wst/article-pdf/52/1-2/167/433777/167.pdf)
average UASB reactor effluent COD for the last two weeks of the trial was 368 mg L\(^{-1}\), which represents a 94.3% reduction of the initial peach canning wastewater COD of ca. 6,500 mg L\(^{-1}\). Post-ozonation of the UASB reactor effluent resulted in a further COD reduction, producing a final effluent with a COD of 55 mg L\(^{-1}\), a total COD reduction of 99.2%. This COD value is well within the South African legal limit (75 mg L\(^{-1}\)) permitted for wastewaters to be discharged to a water system (Water Research Commission, 1987b). These results compare favourably to those of other authors (Benitez et al., 1999; Martín et al., 2002), finding that pre-ozonation of wastewaters resulted in improved biodegradability during anaerobic digestion, and increased the methane production rate.

Conclusions
Ozone as a pre- or post-treatment to anaerobic digestion was shown to be successful in that total COD removal efficiency was increased. Ozonation of wastewaters alone was less effective in reducing the COD than anaerobic digestion by UASB. Ozonation as a post-treatment to UASB was less effective than using ozonation as a pre-treatment to UASB. Ozone as a pre- and post-treatment to UASB, however, achieves the best results in reducing the COD of the wastewaters. It was also shown that the long-term use of pre-ozonated wastewater as UASB substrate did not inhibit the anaerobic digestion process and improved the COD removal efficiency of the UASB reactor, while also increasing the methane production. Final COD values of UASB reactor effluent after pre- and post-UASB ozonation, were well below the South African legal limit (75 mg L\(^{-1}\)) for discharge of wastewaters to a water system.

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