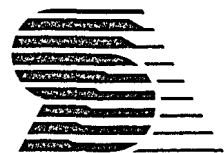


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OXIDATIVE TREATMENT OF A WASTE WATER STREAM FROM A MOLASSES PROCESSING USING OZONE AND ADVANCED OXIDATION TECHNOLOGIES

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Abstract

The discoloration of a biologically pretreated waste water stream from a molasses processing by ozonation and two advanced oxidation processes (O_3/H_2O_2 and O_3/γ -irradiation, respectively) was studied. Colour removal occurred with all three processes with almost the same efficiency. The main difference of the methods applied was reflected by the BOD increase during the discoloration period. By ozonation it was much higher than by AOPs but it also appeared with AOPs. AOPs were, therefore, not apt for an effective BOD control during discoloration.

Introduction

Oxidation of organic pollutants in water is an attractive method of treatment because, if carried to completion, it results in conversion of the organics to innocuous material such as carbon dioxide and water (so-called "mineralization").

Ozone is known for its high oxidation potential. Nevertheless, with refractory substances in waste water it has only demonstrated significant potential for partial oxidation. However, even when the process is not carried to completion partial oxidation usually results in products with enhanced biodegradability and enables by that the removal of biologically resistant compounds in a two stage process consisting of oxidation with subsequent biodegradation.

Advanced oxidation is supposed to have the potential to carry the original organic contaminant through a series of increasingly oxidized intermediates to carbon dioxide. Such a complete mineralization is desirable in a water-polishing operation because it is a single stage process without any residual to dispose of. However, with regard to economy advanced oxidation processes (AOPs) in waste water are almost always in competition with the ozone/biodegradation coupling.

Preliminary investigations with effluents from a molasses processing have indicated that the biologically resistant compounds of this waste stream can be oxidized by ozone and by advanced oxidation as well (Haberl et al., 1993). In this study, both the above methods were

investigated. The primary purpose was to find conditions for the discoloration of the brown coloured waste stream with the challenge to hold the BOD level below 20 mg/L, the limit value of emission in Austria.

Experimental

All experiments were carried out with an effluent from a molasses processing which has already passed a multistage biological treatment. Even after the biological treatment the waste water stream is still deep brown coloured (Absorbency at 435 nm with 1 cm layer: 0.7) and organically high loaded: Chemical Oxygen Demand COD ~427 mg/L; Dissolved Organic Carbon DOC ~148 mg/L; Biological Oxygen Demand (5 days) BOD₅ between 5 - 16 mg/L (BOD₅ will be denoted in the following with BOD only); pH ~8.3.

All laboratory bench test procedures were performed using the assemblage as shown in Figure 1.

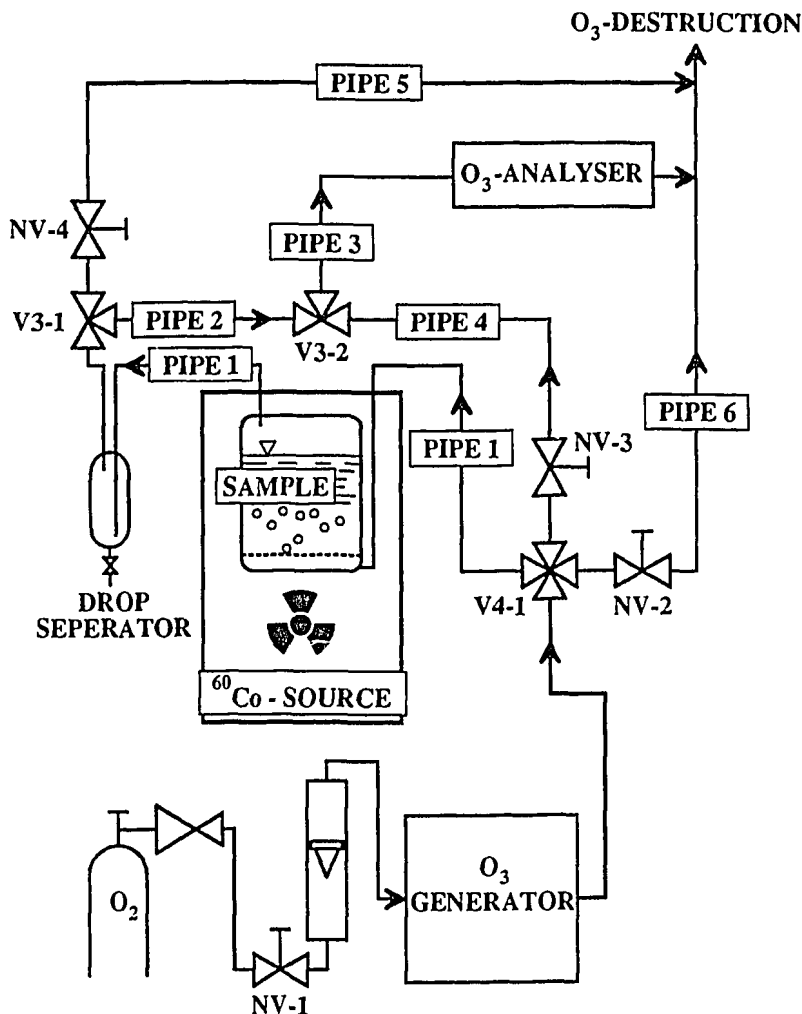


Figure 1. Flow diagramm of the bench-scale equipment (NV needle valves; V4 four-way acting valve; V3 three-way acting valves).

It works as follows:

- START-phase: Sample container is always outside the Cobalt-60-source. Four-way valve V4-1 opens pipe 4 and the three-way valve V3-2 is open to pipe 3. Needle valve NV-3 has been already adjusted before to a gas flow of 1 L/min. (Ozone inflow measurement)
- PROCESS-phase: V4-1 opens pipe 1, V3-1 opens pipe 2 and V3-2 opens pipe 3. (Ozone outflow measurement).

With this equipment waste water can be treated with O_3 alone, O_3/H_2O_2 and O_3/γ under identical conditions. For the O_3 - and O_3/H_2O_2 -treatment processes, respectively the sample container remains outside the Cobalt-60-source. H_2O_2 addition to the waste water is done before filling the sample container. In the O_3/γ -irradiation treatment the switch over from START to PROCESS is performed while the sample container is introduced into the radiation field of the Cobalt-60-source.

In each experiment 1.5 litre of waste water has been treated. The construction of the sample container has been already described elsewhere (Haberl et al., 1993).

Ozone was generated from high purity oxygen in a Sander ozone generator using the following conditions:

ozonated gas production: 60 L/h
 ozone concentration in gas: 108 mg/L

A process photometer (Sigrist model KAS 500) was employed to detect continuously the ozone concentration in the oxygen flow. The total consumption of ozone was calculated through mass balance between ozone inflow and outflow. Other measured parameter included COD, BOD and Absorbency at 435 nm.

Hydrogen peroxide was added as 30% in weight solution (Merck p.A.).

γ -irradiation during ozonation was performed in an AECL "Gammacell 220" Cobalt-60 irradiation source at an average dose rate of 133 Gy/min. (The unit of the radiation dose is 1 Gray (Gy). 1 Gy = 1 J/kg).

In our preliminary experiments (Haberl et al., 1993) we found that in the combination O_3/γ -irradiation a dose of 5 kGy reduced the COD by one order of magnitude. Therefore, 5 kGy was defined to be the maximum dose in the present study. Because 5 kGy corresponds with 37.5 min irradiation time the interval until 37.5 min was the third fixed parameter beside ozone concentration and gas flow (see Experimental) in all the experiments.

An experimental plan was developed with the following objectives:

- determine a proper ratio of H_2O_2 to O_3 for different contact times;
- determine the ozone consumption of all three treatment processes;
- determine the effect of the different treatment processes on COD, BOD and A (at 435 nm).

Results and Discussion

To find the proper $\text{H}_2\text{O}_2/\text{O}_3$ ratio H_2O_2 was added to the waste water and the ozone demand as a function of time was recorded. The example given in Figure 2 shows that the moment of total H_2O_2 consumption is clearly indicated by a distinct drop down in the ozone consumption curve. Like this the necessary H_2O_2 concentration for every contact time could be easily determined now.

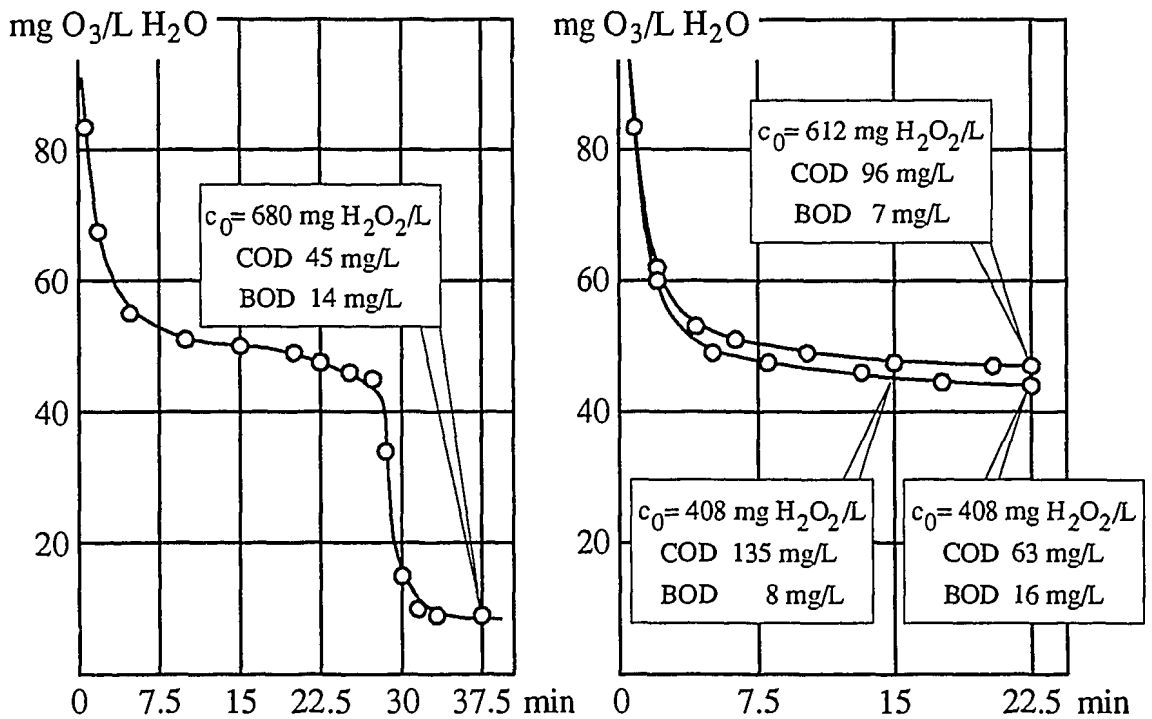


Figure 2/3. Ozone consumption of the waste water as a function of time and initial hydrogen peroxide concentration.

During some of these experiments COD and BOD values were determined at different moments when H_2O_2 was not entirely consumed but still present. The results shown in Figure 3 indicate a relation between the H_2O_2 residual and the sum parameters COD and BOD as follows: Higher H_2O_2 residual concentration causes low BOD values, decreasing H_2O_2 concentration in the waste water increases the BOD again. This can be seen by comparing the 15 and 22.5 min values of the 408 ppm initial H_2O_2 concentration results as well as by comparing the 408 ppm and 612 ppm initial H_2O_2 concentration results at 22.5 min. However, low BOD values result in higher COD values, This follows from the results obtained with 408 ppm initial

H_2O_2 concentration: The BOD after 15 min is half of the BOD found at 22.5 min but the corresponding COD values show just the opposite: the COD after 15 min is almost twice the COD value after 22.5 min treatment. The values obtained with 612 mg/L initial H_2O_2 concentration after 22.5 min corroborate these findings when compared with the values at 22.5 min and 408 mg/L initial concentration. It should be mentioned here that H_2O_2 addition without ozone had no significant effect on the BOD; it, of course, increases the values of COD when added in higher concentrations.

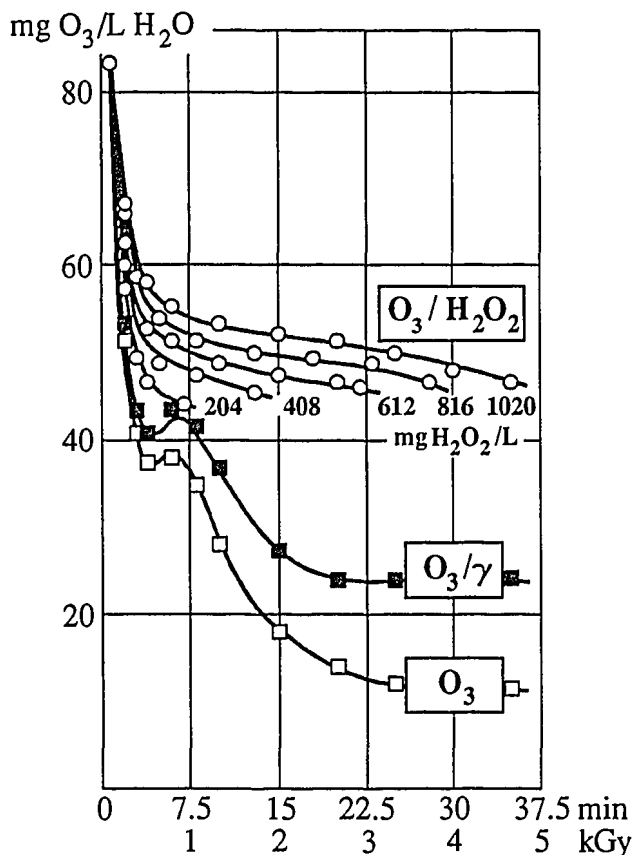


Figure 4. The ozone consumption of the waste water stream during different ozone treatment processes as a function of contact time

The ozone consumption of the three methods applied is quite different (Figure 4). At a contact time of 37.5 min the corresponding ozone consumptions are: 808 mg O_3/L (ozone alone), 1143 mg O_3/L (ozone/ γ -irradiation) and 1932 mg/L (ozone/hydrogen peroxide). Accordingly combined $\text{O}_3/\text{H}_2\text{O}_2$ consumes about 140% more ozone than ozone treatment alone while combined O_3/γ only needs 40% more than sole ozonation. Calculation of the $\text{O}_3/\text{H}_2\text{O}_2$ ratio results in values of 0.79 (molar) and 0.55 (per weight), respectively which are quite common with combined $\text{O}_3/\text{H}_2\text{O}_2$ treatment.

Discoloration of the waste water proceeds very rapidly with ozone as well as with the combined ozone methods. It was sufficient after 7.5 min. The residual absorbency at that time obtained with all 3 methods was about 0.02.

Figure 5 shows now the effect of the different treatment processes on COD and BOD. Because these values changed in the untreated waste water a little bit with time (although it was stored at +4°C) the results have been normalized to actual initial concentrations. A comparison of the COD reduction by O_3 alone and by O_3/γ results in some advantage for the latter when the same contact time is considered but there is a small difference only when the same ozone consumption is the base of comparison. However, this is not valid for combined O_3/H_2O_2 . While the same contact time results in almost the same COD reduction for both combined treatment processes the ozone utilization of the combined O_3/H_2O_2 is worse even when compared with ozonation alone. Just an example: an ozone consumption of about 808 mg O_3/L is recorded after 37.5 min (O_3 alone), 23 min (O_3/γ) and 16 min (O_3/H_2O_2), respectively. This corresponds with the following COD reductions: 71 % by ozone alone (which means 3.1 mg O_3 /mg COD); 77% by O_3/γ (means 2.7 mg O_3 /mg COD) and 63% by O_3/H_2O_2 (means 3.8 mg O_3 /mg COD).

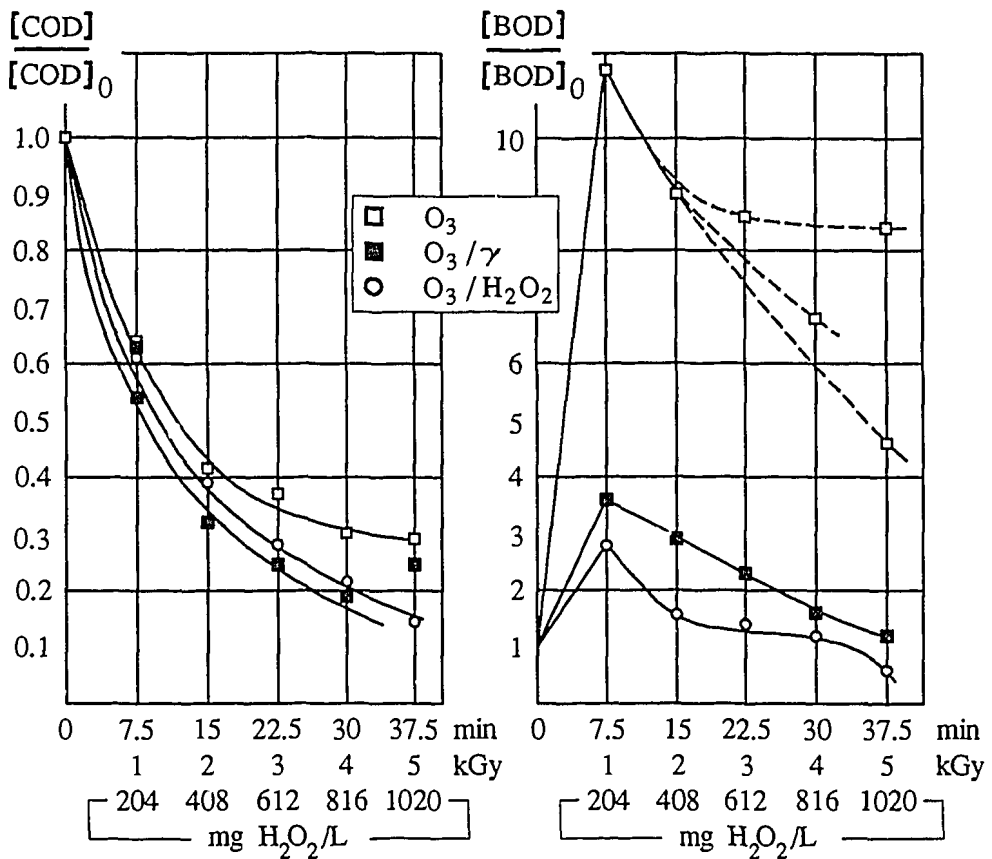


Figure 5. The changes of COD and BOD by ozonation and AOPs, respectively as a function of time.

Figure 5 also shows that the significant differences between the various methods applied are not so much reflected in the COD but in the BOD changes. Especially during the discoloration period ozonation alone produces a much higher BOD increase than the both combined O_3 methods do. Unfortunately the BOD values for O_3 alone after longer contact times scatter enormously. No statement concerning the rate of BOD decline can be made, therefore.

There is also a BOD increase with both combined treatment processes but much less than with ozonation alone. Here again the BOD growth occurs during the discoloration phase and is, therefore, most likely also caused by direct ozone reactions. At the beginning the coloured substances which should react with ozone by direct reactions are present in such concentrations that they can succeed in the competition with ozone decomposition reactions. However, simultaneous generation of hydroxy free radicals causes a reduced BOD increase by two effects: (□) there is now less ozone available for direct ozone reaction and (□□) the hydroxy free radicals react preferably with the biodegradable substances formed via direct ozone reactions. By that both effects prevent formation and accumulation of biodegradable substances to some extent.

This assumption is supported by results obtained with different H_2O_2/O_3 ratios (Table 1). These experiments were performed after the BOD of the waste water had been already dropped down to about 5 mg/L. BOD measurements in such a range are not very accurate. The BOD results given in Table 1 should be understood more as a trend indication, therefore.

Table 1: COD AND BOD AS A FUNCTION OF O_3/H_2O_2 RATIO.

Contact time min	O_3 Consumption mg/L H_2O	H_2O_2 Initial Conc. mg/L	H_2O_2 (mg)	Changes in %	
			O_3 (mg)	COD	BOD
15	709	408	0.58	-61	+60
22.5	1066	408	0.38	-83	+300
22.5	1123	612	0.55	-73	+40
37.5	1932	1020	0.53	-86	-60
37.5 *	1481	680	0.46	-88	+280

* H_2O_2 already consumed after about 28 min; between 28 min until 37.5 min only ozonation happened.

According to Figure 3 an initial H_2O_2 concentration of 408 mg/L is sufficient for a contact time up to 22.5 min. However, for such a contact time a relatively low H_2O_2/O_3 ratio is calculated, i.e. comparatively small steadily declining amounts of H_2O_2 are available after 15 min contact time. As a consequence the BOD significantly increased and the COD reduction simultaneously improved. This may be attributed to direct ozone reactions which can become predominate again when less H_2O_2 is present. If the initial H_2O_2 concentration is enhanced to 612 mg/L a ratio of 0.55 results for a contact time of 22.5 min. The corresponding BOD and COD changes fit well to the appropriate ratio of 0.58 at 15 min contact time.

Although the experiments with 680 mg/L initial H_2O_2 concentration represent a combination of AOP (until 28 min) with sole ozonation (28 to 37.5 min) the results may be interpreted

in the same way: As long as H_2O_2 is present the BOD is more or less controlled and kept down to a certain level by the AOP. After 28 min only ozonation remains which causes BOD enhancement and additional COD reduction. A $\text{H}_2\text{O}_2/\text{O}_3$ ratio related to 37.5 min may be calculated with 0.35 (in spite of the inadequate H_2O_2 addition). The BOD and COD changes recorded in this experiment fit almost exactly to the 0.38 ratio values obtained with a pure AOP at 22.5 min. This is somewhat surprisingly because it indicates even after 28 min the presence of substances able to react with ozone by direct reaction. However, these reactions seems to be easily suppressed by competitive AOPs what is demonstrated by the results obtained with an initial H_2O_2 concentration of 1020 mg/L at 37.5 min.

In this experiment the BOD is even reduced below the concentration at the start of the oxidation treatment. It seems conceivable here to control the BOD exactly via the $\text{H}_2\text{O}_2/\text{O}_3$ ratio and even possible to adjust it just below the limit value of emission to attain maximum COD reduction. This kind of BOD control only works when the AOP is dominant and able to suppress the direct ozone reactions. This is not true for the discoloration period in which such a control would be of great practical use. During this period the organics are simultaneously decomposed by direct ozone reactions as well as by hydroxy free radicals (AOP) and this competition controls the resulting BOD. A promotion of the AOP would decrease the BOD but is hardly applicable.

Summary

Bench scale experiments with a biologically pretreated waste water stream from a molasses processing demonstrated that ozonation as well as AOPs are able to remove the deep colour within minutes. Beside discoloration COD reduction and BOD increase occurred in different amounts depending on the treatment applied. Ozonation alone increased the BOD much more than AOPs did; in both processes the BOD passed a maximum when most of the colour was already removed.

The BOD enhancement in the AOP is attributed to direct ozone reactions. At the beginning the coloured substances which should react preferably with ozone by direct reactions are obviously present in such high concentrations that they can prevail in the competition against the ozone decomposition reactions of the AOP. During this period the resulting BOD is controlled by this competition which is more or less fixed. After discoloration the AOP becomes predominant. The BOD is decreased and can be controlled now via parameters of the AOP. However, the range in which this control can be applied is of less interest for practical use.

Reference

R. HABERL, W. URBAN, P. GEHRINGER, H. ESCHWEILER, "Oxidation of Industrial Waste waters Containing Non-biodegradable Constituents by Ozone with and without Simultaneous Irradiation", Proc. 11th Ozone World Congress, San Francisco: S-10-1 to S-10-12 (1993).

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