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Studies on Disinfection and Chemical Oxidation with Ozone and Chlorine in Water Reclamation*

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Abstract

Laboratory studies showed that *Pseudomonas aeruginosa*, *Aeromonas hydrophila* and *Acinetobacter anitratum* are more resistant to chlorine and ozone than *Escherichia coli*. *Pseudomonas aeruginosa* was the most resistant of all strains tested and was selected as test organism for pilot plant studies on the efficiencies of chlorine and ozone disinfection. The disinfectants proved equally efficient for the disinfection of chlorine demand-free water but ozone was much more efficient in the case of water with a chlorine demand. This difference was confirmed to be due to the property of chlorine to react with nitrogenous substances to form chloramines which are less efficient disinfectants than chlorine. Ozone does not share this property. Laboratory studies showed that ozone was highly efficient in the chemical oxidation of the pesticides parathion, fenthion, lindane and dieldrin and the detergents Manoxol OT and LAS. These compounds are not oxidized under conventional conditions of chlorination. Consideration of the above findings and other advantages and disadvantages of chlorine and ozone accentuate the value of using appropriate combinations of disinfectants for the treatment of certain waters. A final treatment sequence of ozonation, activated carbon filtration and chlorination may improve costs and efficiency of water reclamation.

Introduction

Efficient and economic disinfection is a basic requirement for the reclamation of drinking water from sewage. In the Stander Reclamation Plant developed by the NIWR (van Vuuren, 1973) chlorine is used for this purpose. One of various disadvantages of chlorine (Wallis, Gerba and Melnick, 1974) is that it readily reacts with nitrogen-containing compounds, especially ammonia, to form chloramines which are less microcidal (Chamber, 1971). Absolute disinfection is guaranteed only at breakpoint chlorination which requires a chlorine:ammonia-nitrogen mass ratio of approximately 10:1 (White, 1972). An alternative disinfectant is ozone, which has various important advantages. Among these are that it does not react with ammonia at ozone dosage levels used for disinfection purposes (Besik, 1973; Gardiner and Montgomery, 1968) which precludes the possible oxidation of ammonia to nitrate as reported by Wynn et al. (1973) and Singer and Zilli (1975). Another advantage of ozone is that it is a highly efficient chemical oxidant (American Chemical Society, 1972). The cost of using ozone would be competitive with chlorine for the disinfection of water containing ammonia or organic material and, in addition, would have other important advantages. This report deals with laboratory and pilot plant studies on the feasibility of applying ozone for disinfection as well as chemical oxidation of refractory organic compounds in the reclamation of potable water from sewage.

Materials and Methods

Laboratory studies on disinfection

All bacterial test organisms used, except *Escherichia coli* E25 (Grabow and Prozesky, 1973), were isolated from humus tank effluent exposed to chlorine or ozone in the pilot plant to inactivate all coliform bacteria and to reduce the total plate count by more than 99 per cent. Test strains were kindly identified by Prof. O. W. Prozesky according to the methods of Frankel, Reitman and Sonnenwirth (1970), Edwards and Ewing (1972) and Buchanan and Gibbons (1974), and were designated *Pseudomonas aeruginosa* CPI, *Aeromonas hydrophila* CPI and *Acinetobacter anitratum* CPI. The organisms in unshaken Difco nutrient broth cultures grown for 18 h at 37°C were washed twice in demand-free sterile deionized water and 4 ml of these suspensions were added to 400 ml of demand-free sterile pH 6 phosphate buffer (Cruickshank, 1985) or pH 10 borate buffer (Geigy, 1962). Prior to the addition of standardized chlorine or ozone solutions the buffer-suspensions had counts of about 5 × 10^5/ml. Care was taken to ensure that apparatus such as pipettes, glass breakers and stirrers had no chlorine or ozone demand (Friborg and Hammerström, 1956).
Stock ozone and chlorine solutions were prepared by bubbling the respective gases through deionized distilled water. Ozone was generated in a laboratory Degremont ozonator fed with bottled oxygen. The disinfection efficiency in the presence of compounds with a chlorine demand was studied by the addition of appropriate quantities of ammonium chloride to the stock solutions. Concentrations of dissolved ozone or chlorine in these solutions were determined immediately after addition to the reactor vessel by means of the DPD titrimetric or colorimetric methods of Palin (1967). Disinfection experiments were done at 11°C in a constant temperature room. Reaction mixtures were stirred at 100 rpm on a Phipps and Bird laboratory stirrer. Disinfection was terminated by sodium thiosulphate neutralization (Friberg and Hammerstrom, 1956). Bacterial counts were done by membrane filtration. Membranes were incubated on MacConkey agar for 18 h at 37°C (Grabow and Nuppen, 1972).

**Pilot plant studies on disinfection**

The sand-filtered water of the Stander Water Reclamation Plant at Daspoort, Pretoria, was used for these studies. Flow diagrams of the Stander Plant and the pilot plant used for disinfection experiments are presented in Figures 1 and 2, respectively. Water to be treated in the pilot plant was stored in a holding tank and the influent to the plant was seeded with test organisms by means of a peristaltic pump. Previously described broth cultures were used for experimentation. In view of the dilution factor involved, these organisms were not washed. The final count of test bacteria in the influent to the pilot plant was about $5 \times 10^4$ m$^{-3}$ and experiments were performed at temperatures which varied from 18 to 25°C. Bacterial counts were carried out as described for laboratory studies.

The pilot plant consisted of two continuous flow-through column reactors which simulate practical conditions of operation. The ozone reactor was based on a W.R. Grace design. Both reactors were of similar concentric multi-tubular design which eliminates back-mixing. The flow rate was adjusted to maintain a hydraulic retention time of 6 min in both the 48 l ozone and 30 l chlorine reactors. Chlorine gas was dosed by means of a model 450 Capital Advance chlorinator. Ozone gas was generated in a model LG-2-L2 W.R. Grace ozonator fed with bottled oxygen. Contacting of ozone gas with water was achieved by means of a gas injector followed by a static mixer. Unreacted exit gas was adsorbed in an ozone trap containing 5 per cent potassium iodide solution followed by a wet-test gas meter. The iodide solution was also used to determine the amount of ozone generated by the ozonator at selected wattage, pressure and oxygen flow rate settings. This was done by bypassing the reactor column and passing the gaseous mixture through the solution. The standard iodometric method (Standard Methods, 1971) was used for calculating the mass of ozone consumed during each experimental run.

Frequent sampling of the influent to the plant and the effluents from the two reactors for counts of test bacteria, and careful control and evaluation of the quantities of disinfectants produced and consumed in experimental runs, made it possible to assess the relative disinfection efficiencies of ozone and chlorine under identical conditions of water quality, bacterial numbers, retention time and reactor design.

**Laboratory studies on chemical oxidation**

Oxidation by ozone of four commonly used pesticides, namely...
parathion and fenithion (organophosphorus compounds) and lindane and dieldrin (chlorinated hydrocarbons), and two detergents, namely Manoxol OT (hard anionic alkane benzene sulphonate compound, ABS) and a linear alkane sulphonate, LAS (soft anionic ABS) was studied. Deionized distilled water was used to prepare appropriate solutions of these substances. Solutions of pesticides were prepared by shaking for 24 h in the absence of solvents which may affect oxidation results. Sodium hydroxide and hydrochloric acid were used to adjust pH levels of these solutions. Test solutions were ozonated in a 100 cm x 4 cm glass reactor column for periods of 3 to 5 min. Ozone gas was diffused through a glass frit at the bottom of the reactor. Foaming of detergent solutions was prevented by addition of a drop of antifoam B compound to the reactor. The amount of unreacted gas and the mass of ozone consumed in the reactor were determined by means of a potassium iodide trap and wet-test gas meter as described earlier. Samples were withdrawn from the reactor before and after ozonation. Pesticide samples were subjected to four serial extractions with hexane solvent. The water to hexane ratio for each extraction was 5:1. After shaking, the hexane was withdrawn and filtered through powdered sodium sulphate. Chemical oxidation of pesticides was evaluated by reduction in pesticide concentration determined by gas chromatography. The latter analyses were kindly done by the South African Bureau of Standards. Oxidation of detergents was evaluated by reduction in detergent concentration determined by gas chromatography. The latter analyses were kindly done by the South African Bureau of Standards. Oxidation of detergents was evaluated by reduction in detergent concentration, which was determined by a methylene blue active substances technique (NIWR Analytical Guide, 1974).

Results

Laboratory studies on disinfection

The concentration-time relationships for 99 per cent inactivation of E. coli E25 by ozone and chlorine in demand-free buffer suspensions at pH 6 and 10 are presented in Figure 3. These relationships were obtained by plotting the percentage survival of the test organism against the time of contact. Ozone was a more effective bactericide than the free chlorine species HOCl and OCI⁻ at concentrations below 0.5 mg/l. At pH 6, ozone was three times more effective than chlorine and at pH 10, 23 times more effective. The efficiency of ozone was less pH-dependent than that of chlorine. Chlorination was ten times more efficient at pH 6 (HOCl) than at pH 10 (OCI⁻) whereas ozone was only slightly more efficient at the lower pH level.

The concentration-time relationships for 99 per cent inactivation of E. coli E25, P. aeruginosa CPI, A. hydrophila CPI and A. anitratum CPI by ozone and chlorine in demand-free buffer at pH 6 are presented in Figure 4. These results show that P. aeruginosa is considerably more resistant to both disinfectants than any of the other bacteria tested. Escherichia coli was the most sensitive. HOCl was slightly more efficient than ozone. At a concentration of 1,0 mg/l, ozone was 136 times as efficient as chloramines for the inactivation of P. aeruginosa.

Pilot plant studies on disinfection

The percentage survival of P. aeruginosa as a function of the ozone or chlorine added in a typical experiment with reclaimed water is presented in Figure 5. These results show that a 7-log order inactivation of the test organism required a chlorine dosage of 32 mg/l but only 8 mg/l of ozone. Ozone was thus four times more effective than chlorine based on dosage levels and about seven times more effective according to actual consumption levels. Ammonia determinations on samples taken before and after ozonation verified the fact that ozone did not react with the ammonia which was present in a concentration of 3.3 mg NH₃-N/l.
Laboratory studies on chemical oxidation

The test reactor containing deionized distilled water without pesticides or detergents consumed about 50 per cent of ozone added. Consequently it was necessary to dose the reactor with excess quantities of ozone in order to obtain appropriate concentrations of ozone for studies on chemical oxidation. Reduction in the concentrations of pesticides in solutions exposed to ozone is presented in Table 1. These results show that complete removal of parathion and fenthion and more than 90 per cent removal of lindane and dieldrin added, was obtained by an ozone consumption of less than 100 mg/l. The efficiency of ozone increased with decreasing initial pH levels of reaction mixtures. All pH levels tended to neutrality after ozonation. A chromatogram of heptachlor pesticide after ozonation is presented in Figure 6 to indicate oxidation products. Table 2 shows that chemical oxidation by ozone of the detergents Manoxol OT and LAS was obtained by an ozone consumption of less than 80 mg/l. Efficiency of oxidation increased with increasing concentrations of the detergents.
Discussion

The laboratory studies on disinfection of E. coli and bacterial strains isolated from chlorine or ozone treated water showed that A. hydrophila, A. anitratum and P. aeruginosa were more resistant to chlorine or ozone than the commonly used indicator, E. coli. Pseudomonas aeruginosa was the most resistant of the strains tested, and the present results and those of other workers indicated that it was more resistant to the disinfectants in question than most enterobacteria and viruses (Engelbrecht et al., 1974) and, consequently, the great majority of pathogenic microorganisms generally transmitted by water (Geldreich, 1972). For this reason P. aeruginosa was chosen as the indicator for pilot plant studies on disinfection. Studies on the absolute inactivation of bacteria and viruses are envisaged and selection of suitable organisms and development of appropriate test conditions for this purpose are in progress. The observation that Acinetobacter bacteria are exceptionally resistant to chlorine and ozone is useful since it is a common inhabitant of surface waters (Buchanan and Gibbons, 1974) and may serve as an indicator in the treatment of these waters.

The laboratory studies showed that there was little difference in the efficiency of chlorine and ozone for the disinfection of chlorine demand-free water. The minor difference in the relative disinfection efficiencies of chlorine and ozone recorded in Figures 3 and 4 was probably due to differences in the accuracy of the methods used for the evaluation of chlorine concentrations. Both laboratory and pilot plant studies demonstrated that in the case of water with a chlorine demand, ozone was a much more efficient disinfectant. The reason for this difference is that chlorine reacts with nitrogen-containing compounds like ammonia to form chloramines which are less efficient disinfectants than free chlorine (Chambers, 1971) while ozone does not react with such compounds (Besik, 1973; Gardiner and Montgomery, 1968). This was confirmed by the observation in pilot plant studies that the ammonia concentration of reclaimed water was extensively reduced by chlorination but not by ozonation. The decrease in the inactivation of the test organism between the

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Initial pH value</th>
<th>Ozone dosed (mg/l)</th>
<th>Ozone consumed (mg/l)</th>
<th>Percent Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parathion</td>
<td>9,8</td>
<td>149</td>
<td>49</td>
<td>2 300</td>
</tr>
<tr>
<td>Parathion</td>
<td>6,5</td>
<td>149</td>
<td>32</td>
<td>2 300</td>
</tr>
<tr>
<td>Fenthion</td>
<td>9,8</td>
<td>149</td>
<td>58</td>
<td>2 450</td>
</tr>
<tr>
<td>Fenthion</td>
<td>7,2</td>
<td>149</td>
<td>37</td>
<td>2 450</td>
</tr>
<tr>
<td>Lindane</td>
<td>9,8</td>
<td>149</td>
<td>97</td>
<td>50</td>
</tr>
<tr>
<td>Lindane</td>
<td>6,9</td>
<td>149</td>
<td>85</td>
<td>50</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>9,8</td>
<td>149</td>
<td>101</td>
<td>1 320</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>6,6</td>
<td>149</td>
<td>81</td>
<td>1 320</td>
</tr>
</tbody>
</table>

1. The lowest limit of detection of the method used was 0,1 µg/l
A hump and the dip of the breakpoint curve in Figure 5 was due to a change in the concentration and composition of chloramines. Adequate disinfection of water with a chlorine demand was obtained only when chlorine was added in sufficient quantities to obtain breakpoint chlorination where compounds containing nitrogen are completely oxidized. At this stage nitrogen gas is liberated and free chlorine becomes available (White, 1972).

In the Stander Water Reclamation Plant chlorine is at present used for disinfection of water which has reached an advanced stage of purification (van Vuuren, 1975). This water usually has a chlorine demand and relatively large quantities of chlorine are required for breakpoint chlorination. Although chlorination is generally still cheaper than ozonation, disinfection costs may be reduced by appropriate application of ozone, possibly in conjunction with chlorine. At the Stander Plant disinfection costs could possibly be reduced by a treatment sequence consisting of ozonation, activated carbon filtration and final application of sufficient chlorine to maintain disinfection in the distribution network. Since ozone had no residual effect, the traces of nitrogen-containing compounds present in the water after carbon filtration could serve a useful purpose by combining with

### Table 2

**CHEMICAL OXIDATION OF DETERGENTS BY OZONE**

<table>
<thead>
<tr>
<th>Detergents</th>
<th>Ozone dosed (mg/l)</th>
<th>Ozone consumed (mg/l)</th>
<th>Before ozonation (mg/l)</th>
<th>After ozonation (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manoxol OT</td>
<td>149</td>
<td>72</td>
<td>0.56</td>
<td>0.24</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>77</td>
<td>2.06</td>
<td>0.26</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>73</td>
<td>3.40</td>
<td>0.20</td>
<td>94</td>
</tr>
<tr>
<td>LAS</td>
<td>149</td>
<td>69</td>
<td>0.67</td>
<td>0.22</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>75</td>
<td>1.42</td>
<td>0.24</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>81</td>
<td>3.00</td>
<td>0.18</td>
<td>94</td>
</tr>
</tbody>
</table>
chlorine to form chloramines, which confer the desired residual effect on the final reclaimed product. This would be in agreement with the practice of adding traces of ammonia to water prior to chlorination in order to obtain a final product containing chloramines, which are more stable than free chlorine and combat contamination for a considerable period of time (White, 1972).

The laboratory studies on the ozonation of selected pesticides and detergents (Tables 1 and 2) illustrated the potential of ozone for oxidation of such chemically resistant organics. These results agreed with the findings of Atkinson and Palin (1972). The 50 per cent consumption of ozone added to the reactor containing deionized distilled water could be due to destruction of ozone by a surface-catalyzed reaction during diffusion through the glass frit (Parry and Hern, 1973) and to accelerated auto-decomposition by mass point application of the ozone (Gomella, 1972). The utilization of ozone could however be improved by proper construction of reactors (Rosen, 1973).

Partial chemical oxidation is normally accompanied by a decrease in the molecular size and molecular mass and a corresponding increase in the solubility of organic substances (Gauntlett and Packham, 1973). However, there is a point beyond which ozonation alone, becomes an inefficient operation for the removal of organics. More complete removal may be obtained by a combination of ozone and activated carbon adsorption as previously suggested. The size distribution of the organics in question and the pore size distribution of the relevant activated carbon determines whether ozonation should precede activated carbon treatment or vice versa. In order to optimize the adsorption process, the objective should be to match the above size distributions with due consideration to the effect of ozonation on solubility and molecular mass of dissolved organics. In view of the growing concern about the increasing numbers and quantities of hazardous compounds with which water resources are polluted (Ozonews, 1974), this matter deserves serious consideration. Studies on improved removal of residual organic substances by combinations of ozone and activated carbon are in progress.

The chemical alterations in the ozonated pesticides and detergents were not investigated. These pesticides may have been transformed into oxidation products analogous to those of ozonated heptachlor shown in Figure 6. It is known that ozonation of detergents may result in partial oxidation and cleavage of the benzene ring which deprives the molecule of its surface active and foaming properties (Evans and Ryckman, 1963). Evidence has been provided that comparable chemical oxidation cannot be obtained with chlorination (Robeck et al., 1965; Buescher et al., 1964). Instead, chlorine has the disadvantage of forming addition and substitution products with many organic substances which impart tastes and odours to water (Atkinson and Palin, 1972) and certain chloramines may be hazardous to the health of man and animals (Rosen, 1971).

Another important advantage of ozone over chlorine is illustrated in Figure 3. These results confirm that, in contrast to ozone, the efficiency of chlorine is highly dependent on the pH level (Kott et al., 1974). The minor difference in the disinfection efficiencies of ozone at pH levels of 6 and 10 is probably due to increased decomposition of ozone at pH 10.

The results of this study and the above considerations of the advantages and disadvantages of ozone and chlorine accentuate the value of applying suitable combinations of disinfectants in the treatment of certain waters (Farkas-Himsley, 1964), and indicate that cost and efficiency of reclamation at the Stander Plant may be improved by appropriate inclusion of ozonation. The construction of a large scale ozone reactor for studies on the application of ozone in the Stander Plant is under consideration.

Acknowledgements

Thanks are due to J. S. Burger, Irmela G. Middendorff and Martella van Zyl for their superb technical assistance. This paper is presented with the approval of the Director of the National Institute for Water Research.

REFERENCES


GAUNTLETT, R.B. and R.F. PACKHAM. 1973. The use of activated carbon in activated carbon treatment or vice versa. In order to optimize the adsorption process, the objective should be to match the above size distributions with due consideration to the effect of ozonation on solubility and molecular mass of dissolved organics. In view of the growing concern about the increasing numbers and quantities of hazardous compounds with which water resources are polluted (Ozonews, 1974), this matter deserves serious consideration. Studies on improved removal of residual organic substances by combinations of ozone and activated carbon are in progress.

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