Ozonation for non-filamentous bulking control in an activated sludge plant treating fuel synthesis waste water

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Abstract
A zero discharge mode of operation at the South African fuel synthesis plants necessitates the infinite recycle of treated industrial waste water. The treatment process incorporates activated sludge units in which non-filamentous bulking and carry-over of solids often occurs. The use of ozone for the control of this non-filamentous bulking was investigated on a 33 ℓ/d small pilot-scale plant. An ozone dosage of 1 g per kg mixed liquor suspended solids per day could reduce the diluted sludge volume index from an average of 125 to about 70 mℓ/g mainly by preventing zoogleal growths, the main contributor to the non-filamentous bulking. The solids losses were reduced from 437 to 194 mg/ℓ. Ozonation in the aeration compartment was more effective than in the sludge recycle.

Introduction

South Africa can be called the treasure chest of the West as far as minerals are concerned. Although the country lacks oil, it has vast reserves of coal and it was a logical course of action to use this coal for the synthesis of fuel oil. The exothermic reactions which are necessary in fuel synthesis require large quantities of process cooling water, a resource which is rather scarce in South Africa, particularly on the inland coal fields where the fuel synthesis plants are situated.

Reuse of all waste waters is essential on these plants and in order to prevent pollution of available fresh water sources, a zero-discharge concept is followed. Water reclamation from some of the waste-water streams offers quite a challenge in this rather unique situation. The waste-water streams can include:

- stripped gas liquor from the coal gasification process, high in phenols and ammonia;
- Fischer-Tropsch acid effluent, containing ca 10 g/ℓ C_2 to C_5 monocarboxylic acids; and
- oily water, i.e. spillages and smaller streams from various sections of the plants (Du Plessis, 1987).

The streams are combined and treated in an aerobic activated sludge process for the removal or organic material. Suspended solids and colloids are reduced in the flocculation/clarification/filtration unit processes. Further treatment includes granular activated carbon adsorption for additional removal of organic substances and anion exchange for the removal of sulphates, chlorides and fluorides before the reclaimed water can be used in the process cooling water system (Buys, 1986).

Difficulties with the water reclamation process include sludge bulking and carry-over of suspended and colloidal material. The flocculation and clarification process units cannot successfully cope with the carry-over, particularly in view of the limitation on the use of coagulants which result in increased salinity loads.

The activated sludge usually contains no filaments, but occasionally fungal filaments of the genus *Geotrichum* occur. Of interest though, is the formation of finger-like zoogleal growths in most sludge particles. These zoogleal growths are most likely at the root of the sludge bulking problem.

Ozone has been demonstrated to prevent bulking successfully and reduce carry-over of solids in sewage treatment (Van Leeuwen and Pretorius, 1988) particularly in nutrient removal activated sludge systems (Van Leeuwen, 1988). Furthermore, it has also been demonstrated that ozone can increase the biodegradability of the organic material in fuel synthesis waste-water (Van Leeuwen, 1987). Ozonation could therefore be expected to improve the activated sludge process. The fact that ozone does not contribute to the salinity justified an investigation into its possible use in biological fuel synthesis waste-water treatment.

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Background

Sludge bulking is a problem in most South African activated sludge plants and occurs all over the world. The cause of bulking is predominantly the result of filamentous bacteria. Very few cases of non-filamentous bulking or fungal bulking are on record. Investigations into the prevention of bulking are therefore geared to prevent the growth of filamentous bacteria. No references on the prevention of any bulking other than that caused by filamentous bacteria could be found. Although the mechanisms for zoogleal or fungal bulking control might be different, it was considered expedient to briefly review the bulking control measures which are presently in use.

Latay *et al.*, 1988 describe the most common remedial and preventative filamentous growth control measures as:

- specific, i.e. the selector reactor approach; and
- non-specific, i.e. the use of selective toxicants.

The former approach is often successful in nutrient removal plants where the cause of the filamentous growth is the competition for readily degradable organic matter. Since such a shortage is highly unlikely during the treatment of fuel synthesis waste water, this approach was not investigated. References to the use of selective toxicants are limited to chlorine, hydrogen peroxide and ozone. Of these, the most commonly used is chlorine.

The earliest reference to the use of chlorine for bulking control is by Smith and Purdy (1936). More recently bulking control with chlorine has been studied by Jenkins *et al.* (1982), Neethling *et al.* (1985) and by Lakay *et al.* (1988). Neethling *et al.* (1985) tested four possible chlorine dosing points:

- into the return activated sludge flow;
- directly into the aeration basin;
- into a separate recycle to and from the aeration basin; and
- into the mixed liquor flow just before the secondary settling tank.

These studies led to the formulation of four parameters that have some influence on the efficiency of bulking control:

- Overall mass dose rate =
- Local dose concentration =
- Local mass dose =
- Frequency of exposure =

The relative importance of each parameter depends, according to Neethling *et al.* (1985), on:

- the presence of chlorine scavengers such as nitrite and ammonia;
- the proportion of filaments to floc-formers;
- the relative growth rates of filaments and floc-formers (the so-called bulking potential); and
- the relative resistance of filaments and floc-formers to chlorine (the so-called survival ratio).

If nitrites are present, sufficiently high chlorine dosages are required to oxidise all nitrites before any disinfective residual is established. This would call for a high local dose concentration. Likewise, in the presence of ammonia, when chloramines are formed, the survival ratio depended on the concentration of chloramines and contact time, but not on the MLSS concentration, making the local dose concentration the appropriate control parameter. When a free chlorine residual was established, the survival ratio was a function of the dose and the MLSS concentration and independent of time, calling for local mass dose as the appropriate control parameter. Neethling *et al.* (1985) also proved that there is a limiting frequency of exposure below which bulking cannot be controlled, the value of which depended on filament growth rates.

The presence of ammonia at 200 to 300 mg/ℓ and the limitation on salinity make the use of ozone, rather than chlorine, a logical choice for use in this water reclamation process. The minimum values of the control parameters can to a large extent give an indication of the required dosage level and point of application. Such values are unknown for ozone and this study was aimed at establishing the dosage requirements for ozone in this particular application.

Experimental

The experimental work was conducted on four identical small pilot-scale plants using waste water from the fuel synthesis plants as feed. The pilot plants were operated in parallel for 2 periods of about 3 months each.

Feed composition

The average chemical oxygen demand (COD) of the feed was 3 920 mg/ℓ and the ammonia-nitrogen (NH_4-N) 273 mg/ℓ. Phosphoric acid was added to the feed for nutrient balancing.

Pilot plants

Each pilot plant consisted of an aerobic activated sludge unit of 44 ℓ divided into three compartments – similar to the full-scale units – as shown in Fig. 1. Waste water was fed with diaphragm pumps at a rate of 33 ℓ/d resulting in a retention time of 32 h. The mixed liquor suspended solids then passed through a settler from which the sludge was recycled by means of peristaltic pumps at a ratio of 2:1.

The oxygen concentration was maintained at between 1 and 2 mg/ℓ by means of porous diffusers at the bottom of all three compartments. A sludge age of 20 d was ensured by wasting 2,2 ℓ of sludge per day. The pH was adjusted to about 7 with sodium bicarbonate whenever it dropped below 6.

Ozone was generated from dried air in a high voltage corona discharge ozone generator. The ozone was introduced into the mixed liquor or return activated sludge by means of porous diffusers.

Two separate experiments were conducted to establish the required dosage and most suitable point of application:

- Directly into the third zone of three of the systems i.e. 13, 26 and 39 mg O_3/h respectively. This provided an overall mass dose rate of 1, 2 and 3 g O_3/kg mixed liquor suspended solids (MLSS) per day based on the unit volume of 44 ℓ together with the 8 ℓ of the settler and a MLSS concentration of 6 g/ℓ.
- Into the sludge recycle stream by introducing 13 mg O_3/h into a 2 ℓ contacting tank through which the recycled sludge passed. The local dose concentration at this point was 4,7 mg/ℓ compared to the local dose concentration of 3,1 mg/ℓ in a parallel experiment where 13 mg O_3/h was dosed in the aeration reactor. The difference is due to the

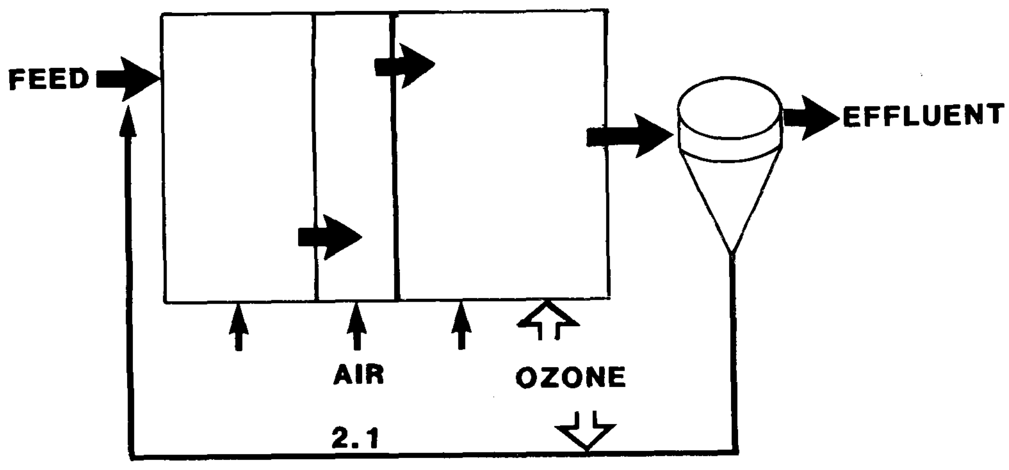


Figure 1
Pilot ozonated activated sludge plant: fuel synthesis waste water

larger volumetric flow rate of MLSS past the aeration reactor dose point compared to the underflow recycle dose point.

The local mass dose rate at 0,53 g O_3/kg MLSS, the overall mass dose rate of 1 g O_3/kg MLSS.d and the frequency of exposure of 1,9/d were not affected by the point of application for the two points tested. The other two possible application points listed by Jenkins *et al.* (1982) i.e. into a separate recycle to and from the aeration basin or into the mixed liquor flow just before the secondary settling tank, were not studied. These application points would require additional equipment which could increase large-scale treatment costs further.

The ozone dosage in each case was calculated by measuring the total quantities of ozone entering and exiting the activated sludge system as a function of time. This value, divided by the total quantity of MLSS in the system, provided the overall mass dosage. Ozone concentrations in air were determined by reacting ozonated air with a potassium iodide solution as described in *Standard Methods* (1980).

Sludge characterisation tests

MLSS values were measured by filtering a 100 mℓ of mixed liquor through a glass fibre filter and determining the mass of the residue after drying at 103°C. Diluted sludge volume index (DSVI) was determined by the ATV (1973) method. This involves measuring the volume occupied by the diluted sludge after settling for 30 min. Dilution should be effected to ensure that the sludge occupies a volume of 20% or just less after 30 min settling.

Microscope studies

A phase contrast microscope was used at 100 times magnification to characterise floc structure and for microphotography.

Effluent and feed quality analyses

The chemical oxygen demand (COD) and the ammonia (NH_4-N) were determined to the guidelines of *Standard Methods* (1980) on filtered effluent samples collected in 25 ℓ containers providing 18 h compounding. Suspended solids were measured by determining the mass of solids left on a preweighted glass fibre filter dried at 103°C after filtering 500 mℓ of effluent.

Results

The results of 2 periods of operation of the pilot plant of about three months each are presented.

Sludge settleability

In all cases ozonation led to an improvement in sludge settleability, except for certain periods after poor operational control had allowed the pH to remain below 6 and even below 5 for several hours. The best results were obtained with an overall mass dose rate of 1 g O_3/kg MLSS.d i.e. at a local dose concentration of 3,1 mg/ℓ. These results are shown in Fig. 2.

The effect of ozone dosed at the same overall mass dose rate but in the sludge recycle is shown in Fig. 3.

The effect of ozonation on sludge microbiology and floc structure

Very few filamentous organisms were normally encountered in

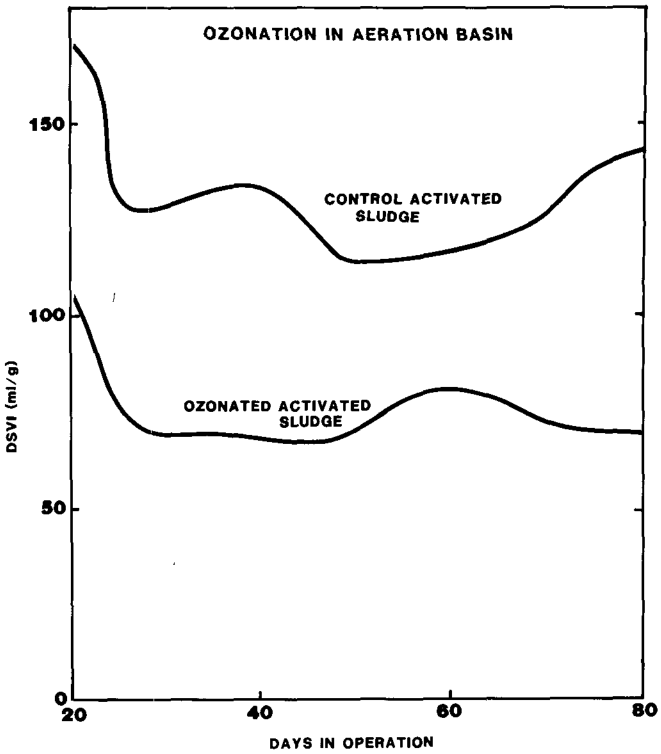


Figure 2
Sludge settling: fuel synthesis waste-water pilot plant

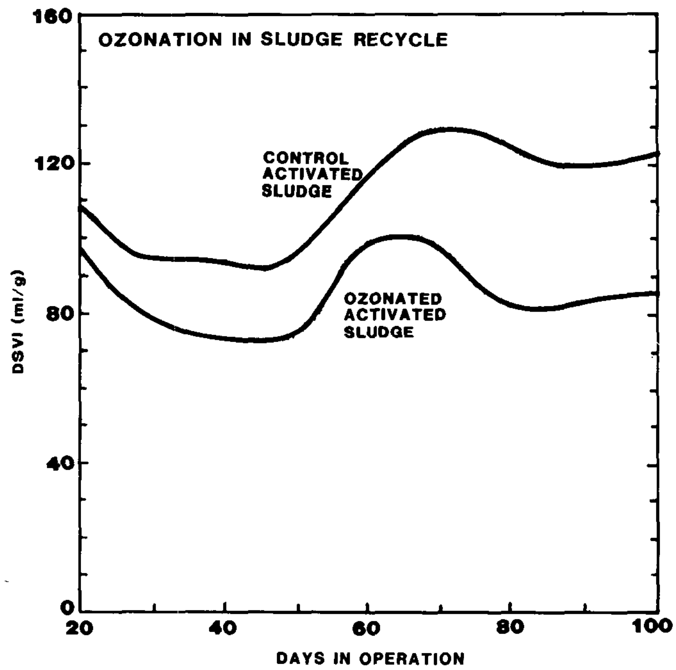
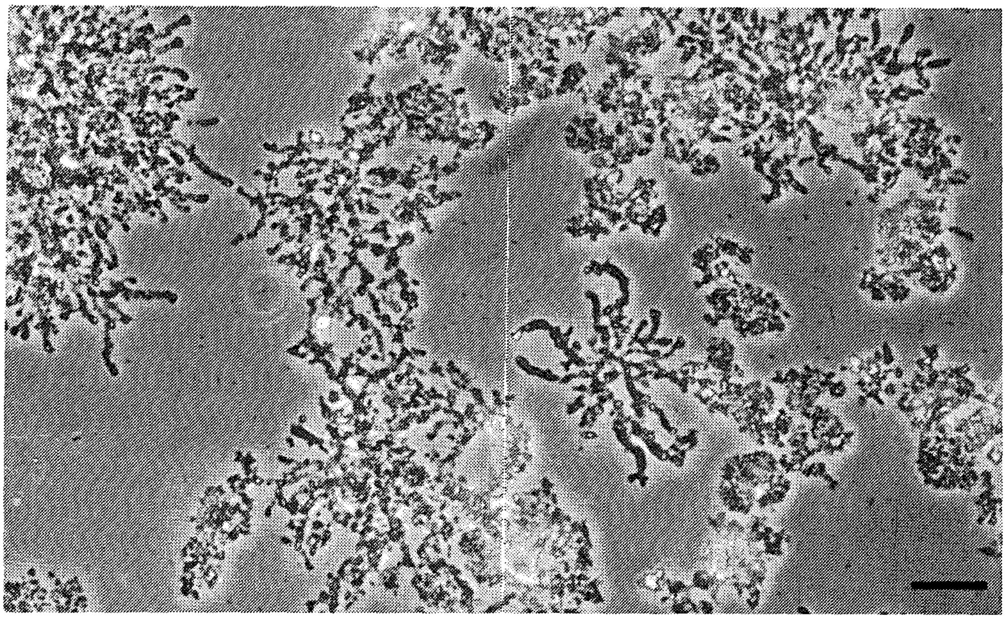
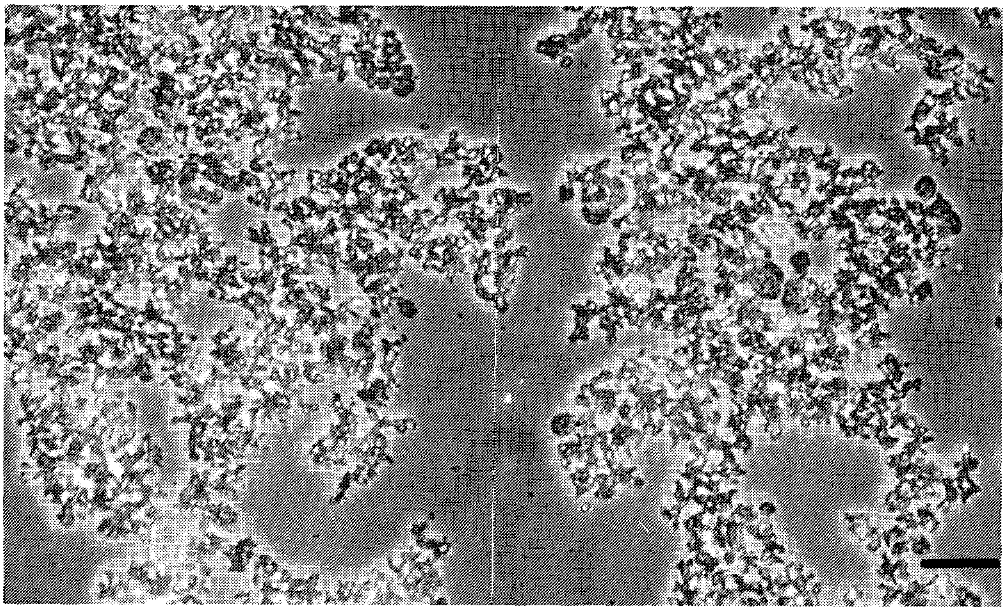


Figure 3
Sludge settling: fuel synthesis waste-water pilot plant



a) Control



b) Ozonated activated sludge

Figure 4
The effect of ozonation on floc structure and microbiology (Bar 100μ)

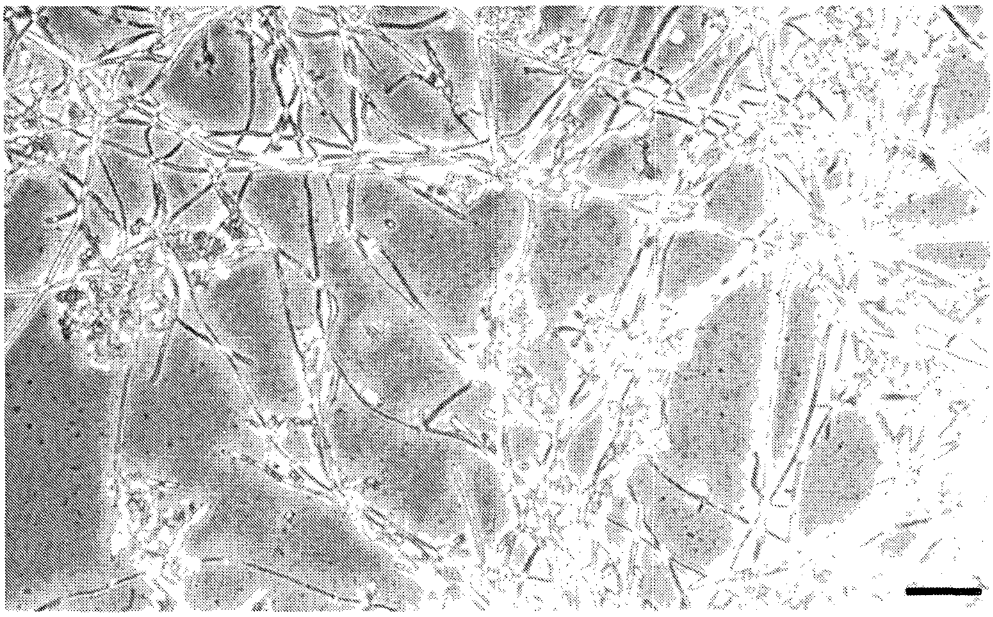


Figure 5
Fungal growths resulting from acidity (Bar 100μ)

the activated sludge. All systems contained free swimming and stalked ciliates and ozonation generally led to an increase in the number of these protozoa.

The control system was characterised by small, loose flocs and a strong tendency to form zoogleal "fingers" (Fig. 4). Ozonation led to a decrease in the occurrence of zoogleal outgrowths and generally to the formation of more compact flocs.

Prolonged exposure to acid conditions favoured the growth of a fungus identified as *Geotrichum candidum* (Fig. 5). These fungi persisted for weeks after the acidity problem had been rectified and were removed by harvesting only, so that it took more than one sludge age to remove the growths. Ozone did not prevent nor rectify this situation, not even at dosage rates of 15 g O_3/g MLSS.d. The DSVI increased sharply to about 210 mℓ/g during the period in which the fungal growths persisted.

Effluent quality

The mean COD of the effluent after biological treatment was 385 mg/ℓ based on 55 filtered samples. On an unfiltered basis the COD was 492 (mean of 12 samples). The mean COD of the effluent from the ozonated plant (3,1 mg O_3/ℓ local dose concentration) was 383 mg/ℓ on 55 filtered samples and 428 on 12 unfiltered samples.

The mean suspended solids concentration in the same unfiltered samples as above was 437 mg/ℓ for the unozonated system and 194 mg/ℓ for the ozonated system.

Discussion

Ozonation had a significant beneficial effect on the sludge settleability. This effect was due to the depression of zoogleal outgrowths by the ozone. Ozonation did not prevent the growth of *Geotrichum candidum* which was always present, but not a nuisance until the pH dropped. A low pH actually favours the growth of *G. candidum* by depressing competing growths (Kuhn and Pretorius, 1988).

Ozonation did not bring about an improvement in the removal of dissolved COD. The ozone dosage was probably too small to significantly influence the biodegradability as found on batch experiments in earlier work (Van Leeuwen, 1987). The improvement in sludge settleability and the formation of larger, denser flocs with fewer pinpoint flocs resulted in a reduction in suspended solids which also led to an improvement in the total (unfiltered) COD. The ozone dosage required was quite small compared with chlorine dosages required for filamentous bulking control i.e. 1 to 15 g/kg MLSS.d according to Neethling *et al.* (1985) and 8 g/kg MLSS.d as found by Lakay *et al.* (1988).

Conclusions

Activated sludge treatment of fuel synthesis waste water can be improved by ozonation in the aeration basin. Ozone, at a dosage of about 1 g per kg sludge solids per day, combats the zoogleal growths which lead to poor sludge settleability and also prevents to some extent the formation of pinpoint flocs which cause a high suspended solids concentration in the effluent.

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