

Thesis Summaries

Denitrification of High Nitrate Wastewater by Anaerobic Filter

The primary aim of the study is the examination of effects of several factors involved in the establishment of an optimum design of anaerobic filter for the denitrification of high nitrate wastewater with nitrate concentration in the range of 500-1000 mg per litre $\text{NO}_3\text{-N}$. Since the cost of methanol, a chemical widely recommended as a reliable and efficient source of organic carbon in anaerobic denitrification, contributes significantly to the operating cost, the possibility of employing brewery waste as an alternative was also investigated.

Bacterial denitrification by anaerobic up-flow filters is applicable as a process for nitrogen removal from high nitrate wastewater. Extremely high removal rates were obtainable, nitrogen removal efficiencies greater than 99% were possible. The filter performance is, however, highly influenced by two basic operating parameters, the feed $\text{COD}:\text{NO}_3\text{-N}$ ratio (indicating the presence of sufficient organic carbon) and the hydraulic loading rate (expressed as the reciprocal of the hydraulic retention time based on the initial void volume). Efficient nitrogen removals are only attainable when the feed $\text{COD}:\text{NO}_3\text{-N}$ ratio is greater than the optimum value (at which efficient removals of both COD and $\text{NO}_3\text{-N}$ occur) and the filter is operated below the critical hydraulic loading rate. The optimum feed $\text{COD}:\text{NO}_3\text{-N}$ ratio was different in the two types of organic carbon source employed, *i.e.* methanol and brewery waste. A higher ratio was obtained in the system using brewery waste, thus indicating a higher organic carbon requirement than the methanol system. This was attributed to

the fact that brewery waste denitrification was characterised by a higher solids production.

The level of the critical hydraulic loading rate was found to be influenced by the voidage of the anaerobic filter. In the present study, using two filters of similar dimensions but packed with two different media [BIOPAC 50E (voidage = 97%) and 38 mm polystyrene spheres (voidage = 51%)], the lower voidage filter could withstand a higher hydraulic loading without undue deterioration in performance. The higher voidage filter exhibited extensive short-circuiting flows at loading rates exceeding 4 per day while the low voidage filter could tolerate a higher loading of 12.5 per day.

The study has highlighted two important operational problems. The first concerned the occurrence of recurrent pressure build-ups, requiring intermittent flushing, in the low voidage filter. Negligible pressure increases were present in the high voidage filter. The contributing factor to the pressure increases was established to be nitrogen gas accumulation and the flushing operation, whose frequency increased with an increase in the loading rate, did not seem to seriously affect filter performance with fast recovery after each flushing. The second problem involved the extensive carry-over of solids into the effluent in the high voidage filter employing brewery waste as the carbon source. This would impose an added requirement of solid separation prior to disposal.

Therefore, the type of organic carbon source used not only affects the organic carbon requirement but also influences the type of operating problem. The preliminary

batch and semi-continuous studies provided a useful appraisal of the two types of organic carbon sources evaluated.

The batch studies not only established that the organic carbon was the more limiting substrate but also provided an insight into the reaction mechanism and intermediates involved. The more complex brewery waste was characterised by the production of volatile acids which tend to counteract the increase in alkalinity which accompanies denitrification. This difference in the buffering capacity also affected the gas composition. The resulting high pH in methanol denitrification tended to shift the carbon-dioxide-bicarbonate equilibrium towards the bicarbonate state, thus giving rise to negligible carbon dioxide in the gaseous phase.

The kinetic coefficients obtained in the semi-continuous studies were reflected in the subsequent filter studies. In the first place the slightly inferior denitrification efficiency of brewery waste to methanol was clearly indicated in the coefficients relating COD to $\text{NO}_3\text{-N}$ removal rates obtained in filter studies, which established a close agreement with the corresponding coefficients obtained in the semi-continuous studies. Secondly, as described earlier, the characteristic high solids yield coefficient of the brewery waste system obtained in the kinetic studies was very much in evidence in the filter studies (extensive solids carry-over in the effluent).

With regard to reactor capacity, for filters of the dimensions employed, a greater percentage of the removal occurred in the bottom section. Examination of the solids revealed a greater concentration at the bottom. The bacterial mass was observed to be mainly trapped within the voids of the packing rather than attached to the medium. The micro-organisms prevalent

within the filter bed consisted chiefly of bacteria and protozoa and there was no indication of the presence of other higher organisms.

Finally, the three-year study has demonstrated that anaerobic filters are comparably simple to operate with negligible control required to achieve efficient performance.

Based on these findings, it is concluded that in order to achieve optimum design it would be necessary to conduct prior pilot-scale studies to determine the applicable critical operating parameters involved.

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Dispersion of Particulate Additives in Rubber Using the Batch Operated Internal Mixer - A Study of Flow Behaviour and Properties of Rubber Mixes

As an aid to understanding the mechanics of mixing in an internal mixer, laboratory-scale trials were carried out using a mixer with a transparent plastics chamber. The use of transparent rubber and coloured 'markers' permitted direct viewing of the characteristic flow patterns derived from the use of three fill factors.

These mixing trials have indicated the rheological properties which must be measured to predict the mixing behaviour of a rubber. Also considerable information is contained in the visualisations which will aid further work in control and instrumentation strategies and in fundamental design/mathematical modelling studies.

A laboratory Banbury mixer and Brabender Plastograph are used to prepare the rubber

compounds which are then characterised for the dispersion of compounding ingredients. For carbon black dispersion studies, several techniques are employed. Capillary rheometry is used to study the stress-strain rate relationships and to obtain die swell, shear and tensile properties. Creep and elongational tests are also carried out on uncured mixes. In addition, measurements on Mooney viscometer, Monsanto rheometer and analysis of bound rubber are made. These tests for filter dispersion are supported by microscopic examination of microtomed sections. Work is also geared to examine properties which are not only sensitive to changes in levels of carbon black dispersion but also those which are readily measured and can be used in industry. Measurements of mechanical phase angle and electrical resistivity are considered. Dispersion of non-black compounding ingredients is studied by X-ray microradiographic technique and analysis of vulcanisate properties.

To relate the performance of the Plastograph and Banbury mix the concept of mixing energy per unit volume of material is used.

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Histological and Biochemical Studies on South American Leaf Blight of *Hevea* Species

Resistance of *Hevea* to a fungal leaf disease, South American leaf blight (SALB) caused by *Microcyclus ulei* (P. Henn.) Arx. could be related to hypersensitive collapse of epidermal and subepidermal cells around entry points of the pathogen. Speed, intensity and frequency of hypersensitive cell collapse were proposed to determine the arrest of

mycelial spread. Conidial germination, germtube penetration and hyphal elongation were similar in all clones tested 12 h after inoculation but later hyphal development slowed down on resistant leaves on which appressorium formation also occurred earlier.

Extracts of leaves from resistant *Hevea* clones were more inhibitory to conidial germination than extracts of susceptible clones. Inhibition was increased by time of incubation of extracts interpreted as due to action of leaf enzymes on phenols. However, the degree of resistance of healthy *Hevea* leaves did not correlate with their total phenol content. Moreover, content of total phenols and ortho-dihydroxy phenols showed little difference in healthy and diseased leaves up to 120 h after inoculation of detached leaves.

Several enzymes were isolated and their roles with SALB development investigated. Indole acetic acid (IAA) oxidase activities of preparations from *Hevea* leaves were stimulated by 2,4-dichlorophenol as well as by naturally occurring phenolics: p-coumaric acid, scopoletin, 4-methylumbelliferone and chlorogenic acid. Kaempferol and quercetin which have been associated with resistance of *Hevea* to SALB were shown to function both as cofactors and as competitive inhibitors of *Hevea* leaf IAA oxidase. Changes in the contents of quercetin or kaempferol or activities of IAA oxidase could be involved in SALB development. Higher activities of IAA oxidase and peroxidase were found in leaves from susceptible *Hevea* clones than resistant ones. Infection especially of resistant leaves stimulated increased activities of IAA oxidase and peroxidase with higher and early detection of the increases occurring in resistant leaves. Lesions in leaf disks suspended on solutions of several growth substances (IAA, kinetin, naphthoxy acetic acid and gibberellic acid) were smaller than

lesions in disks suspended on water. Diseased susceptible leaves suspended on IAA solution also possessed higher IAA oxidase and peroxidase activities than diseased leaves suspended on water. The increase in enzyme activities might be related to the smaller lesions developed on disks suspended on IAA solutions. There was no direct correlation between activities of polyphenol oxidase, B-glucosidase and pectinmethylesterase of healthy *Hevea* leaves with resistance. B-glucosidase activities were higher in infected leaves, especially susceptible ones, while changes in activities of polyphenol oxidase and pectinmethylesterase showed slight difference between inoculated susceptible and resistant leaves.

The process of abscission of diseased *Hevea* leaflets infected with SALB seemed to differ from senescent, debladed or ethylene-treated leaves in that cell division layers

which occurred in ethylene-treated, debladed and senescent leaves were absent in heavily infected leaves. Indole acetic acid inhibited petiole stump abscission of debladed leaflets but not infected leaflets. Indole acetic acid oxidase and peroxidase activities were higher in infected leaflets and in tissues around the abscission zones. Changes in pectinmethylesterase activities could be associated with abscission of debladed or ethylene-treated leaflets but the association was less convincing in the abscission of diseased leaves.

The results obtained were in accordance with the suggestion that resistance of *Hevea* to SALB was biochemical rather than morphological in nature.

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