

EXECUTIVE SUMMARY

1. BACKGROUND AND MOTIVATION

Eutrophication is a natural process that is greatly aggravated by the action of man in the natural environment. Deterioration of South Africa's natural water resources results directly or indirectly from the discharge of industrial effluent rich in nutrient nitrogen and phosphorus. The South African edible oil refineries generally discharge poor quality effluent, which causes threat to the water resources and wastewater treatment installations.

The edible oil industry has been identified to be amongst the 75 industrial groupings in South Africa. In all, there are about 16 edible oil-processing plants, run by 10 separate groups. These industries refine and process approximately 300 000 tons of crude vegetable oil per year, which increases annually by about 3%.

Edible oil effluent entering the sewer system consists mainly of fats, oils, greases (FOG), sulphate and phosphates resulting in both high inorganic and organic loadings at the respective wastewater works. Often effluents from edible oil industries entering wastewater systems have been pretreated to remove most FOG, however due to their natural triglycerides structure not all FOG is removed. In this regard it is noted that previous studies have shown that fatty material within waste streams from food industries are readily biodegradable and it, therefore, follows that these effluents are amenable to biological treatment.

2. STATEMENT OF OBJECTIVES

The research proposal submitted, and accepted, by the Water Research Commission detailed the objectives of the research which are as follows:

- To investigate the source of effluent production during the different stages of refining
- To chemically characterise the effluent

- To assess the efficiency of aerobic biological treatment for the removal of chemical oxygen demand (COD) and phosphate in the final effluent.
- To apply techniques for anaerobic digestion with retention of biomass for the treatment of vegetable oil effluent;
- To study the dynamics of anaerobic biodegradation of the lipid and non-lipid fractions of vegetable oil effluents;
- To develop a treatment protocol for on-site combined aerobic-anaerobic biological treatment of vegetable oil effluent.

Revised objectives:

- Due to time constraint, all research will be conducted at a laboratory scale and not pilot scale onsite.

From the, abovementioned, objectives it can be seen that the major aim of the project was to investigate the relationship between microbial activity and the three primary functions of a biological wastewater treatment facility viz., carbon (both aerobically and anaerobically), nitrogen and, phosphorous removal. Although, initially the main thrust of the research focused on biological phosphorous removal, the emphasis changed to mainly COD and FOG removal. This change was necessitated by alterations made on an operational level. The chief industrial partner in this research switched from a phosphoric acid based refining method to using caustic soda as an alternative method for oil refining. Therefore, the effluent phosphorous concentrations decreased dramatically and the need for biological phosphorous removal, prior to discharge, was made unnecessary, although, the need for COD and FOG removal remained a priority. For example, following this change, and decreases in phosphorous concentrations, resulted in all experiments requiring dosing with di-potassium hydrogen phosphate (K_2HPO_4) to enhance biological activity.

3. SUMMARY OF RESULTS AND MEETING OF OBJECTIVES

The main aim of this study was to assess the capacity of a laboratory scale effluent treatment process that will produce final effluent having a regulatory acceptable organic load and phosphate concentration prior to its discharge into the municipal sewer system. The study was conducted in various stages including: wastewater characterization,

treatability studies, and laboratory scale organic and nutrient removal treatment investigations.

With regards to the phosphorous removal objectives, following analysis for various effluent parameters, treatability studies were conducted using an aerobic-anaerobic sequencing batch reactor with a total hydraulic retention time of 24 hr. The results showed an average of 75% reduction of COD and more than 90% removal of FOG. Based on the results of effluent characterisation and treatability studies, a laboratory scale activated sludge effluent treatment process was designed and operated with two bioreactors (aerobic and anaerobic) in series. The system was operated for a period of 1 month resulting in 70% removal of COD and 4% phosphate reduction. After some structural and operational changes from the original design configuration, the system was the operated continuously for the duration of the study period. An optimum COD removal of 75% and 107 mg/L phosphate reduction was achieved during the last operational phase of the system. More than 95% reduction in FOG has been achieved in both semi-continuously and continuously operated systems.

In order to evaluate the effect sludge age has on biological phosphorus removal in oil effluent and to determine the optimum sludge age, a sequencing batch reactor was set up for the experimentation. The effluent was exposed to alternating anaerobic and aerobic conditions. The reactor had a hydraulic retention time of 12 hr. Sludge ages of 5, 10, 15 and 20 days were used. The COD, phosphorus levels, mixed liquor suspended solids, nitrates and ammonium levels were determined. The 10-day sludge age proved to be most effective in phosphorus removal and a removal efficiency of 84% was obtained. These experiments also indicated the complex interactions between design criteria and physiological requirements of the microorganisms. For example, initial anaerobic reactor volumes and hydraulic retention times showed a significant effect on subsequent microbial activity.

Additional experiments were made to optimise conditions for prefermentation in order to obtain the highest concentration of Volatile Fatty Acids (VFA's) to improve biological phosphorus removal from edible oil effluent. The conditions that were optimised were the hydraulic retention time, the effect of adjusted and natural pH and effect of mixing and

non-mixing. A single stage laboratory scale 10 L Primary Acid Fermenter Sequence Batch Reactor was set up for determination of hydraulic retention time. 4 x 1 L conical flasks were used as batch reactors for determination of total solids, pH and mixing effects. The laboratory scale results showed that an 8 day time period, 12 hr hydraulic retention time, a total solids concentration of 3 000 mg/L and adjusted pH to 7.0 with mixing showed optimum VFA production. When the optimised system was combined with a Biological Phosphorus Removal Sequence Batch Reactor, a 76% COD reduction and 78% phosphate reduction was achieved therefore it can be concluded that a prefermentation stage improves biological phosphorus removal from edible oil effluent.

The vegetable oil industry produces effluent containing quantities of fat, oil, sodium, phosphates as well as other pollutants. Physico-chemical treatment methods, such as Dissolved Air Floatation (DAF), gravity separation and the use of coagulants have been attempted providing a considerable reduction in organic loading; however, discharge standards are still not met. Thus, biological treatment methods are being sought after. Aerobic treatment has been attempted however, shock loads cause problems while running such a process. The objective of this phase of the study was to assess the efficiency of anaerobic digestion technology to degrade vegetable oil effluent as well as the efficiency of the Anaerobic Baffled Reactor. Anaerobic digestion involves the breakdown of organic matter by the action of microorganisms in the absence of oxygen, producing methane-rich biogas. The oil effluent was characterized, providing significant information on its chemical composition. It was found that the effluent had high sulphate content as well as a high COD. The high sulphate content of wastewaters has known to promote growth of Sulphate Reducing Bacteria, which utilize the same energy source as Methane Producing Bacteria and therefore compete for the same energy source. Sulphate and lipid reduction pretreatment experiments were carried out, using barium chloride and gravitational separation respectively. The results obtained, showed that the use of barium chloride to reduce sulphate content in oil effluents was successful, with significant sulphate reduction. The lipid reduction experiments however, did not show any significant lipid reduction. Batch tests were conducted in serum bottles to assess the extent of biodegradation of the oil effluent in its raw state as well as with reduced sulphate content. Methanogenic toxicity tests on the raw and pretreated oil effluents provided a range of toxicity results. These assays are relatively simple and inexpensive. Gas

production was monitored to determine the rate and extent of biodegradation. The efficiency of digestion was assessed by COD reduction. Results indicated potential inhibition of the methanogenic bacteria responsible for methane production by the presence of a toxic substance or substances (at elevated concentrations) in the oil effluents. Results showed raw effluent to be more susceptible to anaerobic degradation. A laboratory scale Anaerobic Baffled Reactor was assessed to treat oil effluents anaerobically and compared to Fed-batch digestion. Both reactors were fed a combination of oil effluents (COD 2000 mg/L) and artificial effluent. Results indicated that anaerobic fed-batch digestion is a promising method of treatment for oil effluents and that the anaerobic baffled reactor is not suitable for treatment of this type of effluent.

For the pretreatment of the effluent, all the results, viewed collectively, seem to indicate that the techniques of ozonation, peroxone and ultrasonics are ineffective methods for the pretreatment of an edible oil effluent.

It has been shown that ozonation performs optimally in the presence of unsaturated bonds (Kloos, 2000). Therefore, with these present in low concentrations, optimum ozonation proved unsuccessful. From all of the pretreatment results obtained it can be concluded that the alternative pretreatment methods were not as effective as the current pretreatment method. Thus, the method of chemical coagulation and flocculation with C40 appears to be the most effective pretreatment from the range of coagulants investigated for the edible oil effluent.

An activated sludge process was designed and the operation was based on a Modified Ludzak- Ettinger (MLE) configuration which was preceded with optimization of appropriate pretreatment technology. The commercial coagulant C40 showed comparatively superior performance and was selected as the pretreatment technology to prepare effluent for activated sludge treatment. The lab scale process was conducted in phases encompassing common operational parameters. Early stages of the lab scale process were unsuccessful since the wastewater was not pretreated. Subsequent to pretreatment, overall performance of the process was good recording maximum COD removal efficiencies of > 90% during steady state conditions. The process responded positively to

increase in the influent COD concentration (organic strength) with the maximum concentration of COD removed being > 1500 mg/L.

Apart from phosphorous removal total organic concentration removal became a critical focus point and in addition various cultures (yeast, molds and bacteria) were isolated from oil- contaminated soil to determine their relative oil degrading capacity.

Bacterial, yeast and fungal monocultures were used individually to determine their ability to grow on an agar medium containing commercial fatty acids (i.e. oleic and stearic acid respectively) as a carbon source and to determine their capabilities in degrading the fatty acid component in edible oil effluent samples which were monitored by COD and FOG analysis. Tests at discrete pH's of 5, 7, and 8 and at temperatures of 21°C and 31°C, respectively.

Results have shown that the isolates belonging to the *Mucor* spp. were capable of growing excellently on the agar plates, while the *Alternaria* spp. grew poorly on both oleic and stearic fatty acid agar plates. For the purpose in this study, FOG collectively represents the triglyceride or long chain fatty acid component present in the edible oil effluent. Using the raw effluent samples, the parameters of pH 5 and temperatures of 31°C, showed that the best FOG removal rates of 90% by the *Alternaria* spp., 89% by both *Mucor* spp. when compared to the other experimental parameters used.

For the bacteria and yeast, isolate F showed a 90% FOG removal at pH 5 at 21°C and *Rhodospiridium* sp showed a 91% FOG removal at 31°C respectively.

4. RECOMMENDATIONS FOR FUTURE RESEARCH

As a result of these studies various areas have been identified for future research. For example, the oil effluent was found to contain amounts of phytosterols, which could possibly be extracted, purified and sold as an animal feed supplement. In order to achieve this, it will be necessary to analyze edible oil effluents from all of the oil refineries over an extended time frame to determine the concentrations of the phytosterols in the different effluent streams, as well, as the extraction potential.

An additional area identified is the need for a comprehensive analysis of the effluent. This is necessary as operational and refinery procedure changes result in significant chemical characteristic changes in the effluents. This, in turn, effects the microbial associations required for further biological treatment of the effluents.

Settling problems as well as changes in microbial interspecies interactions have been noted in the pilot-scale activated sludge system. Further research will be required to determine the complex interactions between the pollutant and microbial associations and their interactions, which are required for effective activated sludge treatment of organic effluents.

5. COSTING ANALYSIS

The costs involved in biologically treating the raw edible oil effluent will include a substantial initial capital expenditure including the design and construction of the BNR process to the specifications required, as well as specialized equipment such as pumps, aerators and mixers. All of these start-up expenses are dependant on the wastewater characteristics of the effluent and will therefore differ according to the industry.

Other costs involved in biological treatment include:

- a) Flocculation using C40, since this is a pre-requisite for biological treatment.
- b) Chemical Consumables, such as H_2SO_4 to reduce the alkalinity of the effluent before flocculation, as well as NH_4Cl and KH_2PO_4 which are used to supplement the flocculated effluent to the ratio C:N:P = 100:10:1 in order for BNR to take place.
- c) Running expenses, especially electricity as it is required for mechanical mixing and aeration of the mixed liquor.
- d) Manpower, the BNR process will require at least one skilled process-controller to operate and maintain the process and 2 or 3 factory workers for maintenance, sampling and cleaning of the reactors in the BNR process.

Table 1: Costs and concentrations of chemical consumables used to flocculate the edible oil effluent.

Chemical	Price	Concentration required	Price/kilolitre
C40	R13.50/kg	8 g/kL	R108/kL
H ₂ SO ₄	R29.20/L	1 L/kL	R29.20/kL
NH ₄ Cl	R66.00/kg	200 g/kL	R13.20/kL
KH ₂ PO ₄	R210.00/kg	40 g/kL	R8.40/kL
Total			R158.80/kL

From Table 1 it can be seen that it would cost R158.80 to flocculate and supplement one kilolitre of effluent.

The following is the formula used by Durban Metro to calculate the relative effluent costs:

$$\text{Cost (R/kL)} = \text{Volume of effluent (kL)} \times 0.334[\text{Average COD (mg/L)} - 350 \text{ mg/L}]$$

The charge only starts at a COD over 350 mg/L; this is the average COD of domestic sewage. The idea is that the weaker effluents attract no charge other than the sewage connection costs.

Table 2: Trade effluent costs according to Durban Metro Wastewater Department for disposal of the various effluents.

Type of Effluent	Average COD (mg/L)	Cost (R/kL)
Raw Effluent	7500 mg/L	R23.88/kL
C40 Flocculated Effluent	1500 mg/L	R3.84/kL
Biologically Treated Effluent	500 mg/L	R0.50/kL

From Table 2 it can be seen that the biologically treated effluent, since having the lowest COD concentration will be the cheapest to discharge at only R0.50/kL. While the costs to discharge the raw and flocculated effluents are much greater and will therefore be R23.88/kL and R3.84/kL respectively.