

REFEREED PAPER

EXPERIMENTAL EFFLUENT TREATMENT AT SEZELA

GENT RD

*PO Box 194, Durban, 4000, South Africa
groy@illovo.co.za*

Abstract

The furfural plant at Sezela generates a unique effluent that is currently discharged into the sea. Although the effluent is essentially dilute acetic acid, it includes other components that render it difficult to treat. Various methods of treatment have been investigated and trialled, including a number of aerobic and anaerobic processes. Recovery of the acetic acid has also been investigated.

A membrane bioreactor (MBR) was constructed at Sezela and has been successful in treating 25% of the effluent from the furfural plant, achieving on average a 95% reduction in chemical oxygen demand. The success of the MBR is due to the high biomass concentration allowed by the membrane technology. At Sezela it operates above 50°C and has very low sludge production. However, due to the high energy costs inherent in the aerobic process, the MBR falls short of a complete solution to Sezela's effluent treatment.

MBR technology is a high rate, compact process that has been successfully applied to domestic sewage and effluent generated by offcrop cleaning, achieving good final effluent quality. Experience has also shown that maintenance is reasonable. It should therefore be taken into consideration by the industry as a possible solution for effluent treatment. However, it has significant advantages over conventional activated sludge plants only where there are space limitations and water re-use is a priority.

Keywords: effluent treatment, MBR, aerobic, anaerobic, acetic acid, domestic effluent

Introduction

The Sezela site consists of the sugar mill with an attached downstream products factory. The downstream factory has a large plant that produces furfural (FF) and a few smaller plants that make other organic chemicals. The FF plant uses bagasse and steam to make FF. The reacted bagasse (residue) is returned to the boilers but the condensed steam leaves the plant as acid water effluent once the FF has been recovered. Sezela therefore experiences a net loss of water and any water recovery from effluent would be valuable. Sezela has two effluent treatment plants – the conventional plant that treats sugar mill effluent, site runoff and local domestic sewage, and the plant that treats a portion of the FF plant acid water effluent.

Both effluent treatment plants treat the wastewater by biological means. This involves using a culture of microorganisms to consume the organic impurities in the effluent. Biological treatment can be aerobic (with oxygen) or anaerobic (without oxygen). The different environments cultivate different microorganisms and thus the treatment characteristics are very different. Aerobic treatment is easier and more stable and so is more commonly used. Aerobic and anaerobic processes will be compared in more detail later. Both effluent treatment plants at Sezela are aerobic.

Aerobic microorganisms require oxygen to break down the pollutants in the wastewater. The amount of oxygen required can be estimated by the chemical oxygen demand (COD). The COD is the mass of oxygen (in mg/L) required to chemically oxidise the pollutants present in the effluent. A more relevant measure is the biological oxygen demand (BOD), the mass of oxygen required to biologically break down the organic pollutants present. However, COD is used more widely as measurements can be taken quickly, whereas BOD measurements take days. The concentration of microorganisms (or biomass) present in the wastewater is also an important consideration. Biomass concentration is generally measured as mixed liquor suspended solids (MLSS), also in mg/L.

This paper will discuss the treatment of the FF plant acid water effluent, starting with the previous work done. The operating MBR at Sezela will be reviewed, and the possible application of MBR technology in the sugar industry will be mentioned.

Description of the FF plant acid water effluent

The furfural plant produces roughly 100 tons per day of furfural (FF) at greater than 99.5% purity. Bagasse is reacted with steam at high temperatures and pressures (see Figure 1). The resulting vapour is condensed giving an aqueous stream with 3% FF and 1% acetic acid. This is then distilled in the azeotrope column to remove the majority of the water and concentrate the FF up to 30%. The FF stream is then further processed to achieve the desired purity. The FF losses to the effluent bottoms are controlled to below 300 ppm. The acidic effluent from the column is sent to cooling towers to reduce the temperature from 100°C to 45°C. It is then sent to the dissolved air flotation (DAF) unit to remove some of the wax and suspended solids. The remaining effluent is then pumped out to a surf outfall. Typical qualities of the effluent pumped to sea are given in Table 1.

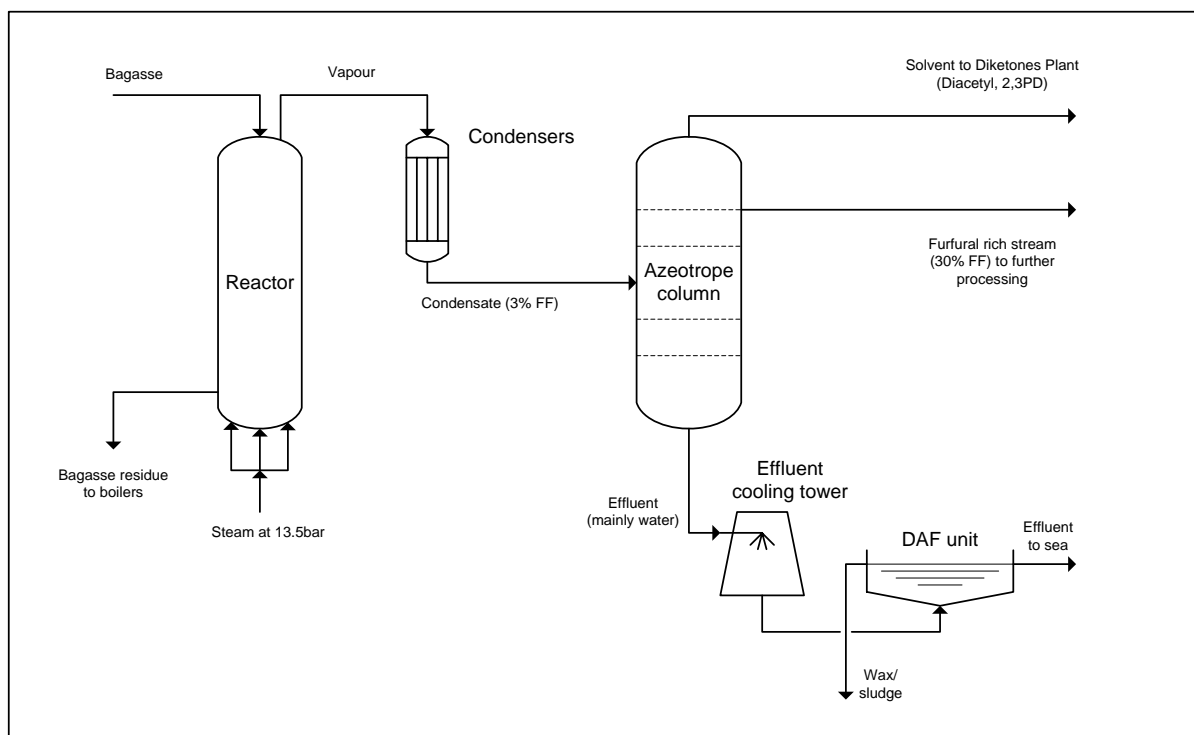


Figure 1. Simplified diagram showing source of effluent.

Table 1. General properties of furfural (FF) plant effluent from the azeotrope column.

Flow	m ³ /ton FF	30
pH		2.8
COD	mg/L	17 000
Acetic acid	wt%	1.2
Formic acid	wt%	0.1
Furfural	mg/L	200
Waxes	mg/L	100

The effluent pipeline discharges close to the shore in the highly aerated area of the surf zone. Aesthetic impacts are limited to a slight yellow plume that can sometimes be seen around the discharge. The environmental impact of the sea outfall has been monitored by the Council for Scientific and Industrial Research (CSIR) and has been found to be minimal, especially in the long term. A study by Blair (2007) concluded that the microorganism population near the discharge was probably equally likely to be influenced by the effluent outfall, the neighbouring estuary or the nearby stormwater drain. However, the status of Sezela's permit to discharge is currently tentative. It is unlikely that Sezela will be permitted to discharge untreated FF plant effluent into the sea indefinitely, and the possibility has always existed that the plant could be forced to close should the permit be refused. This places some pressure on finding a solution for the treatment of the effluent. The discharge of effluent also affects Sezela's water balance. This is because the steam fed to the reactors (typically 140 t/h in total) is essentially pumped out to sea as effluent, instead of being returned to the boilers as condensate. Treatment of the effluent is therefore an opportunity for water recovery, which would improve Sezela's water balance and reduce water costs. Further opportunities exist in possibly recovering the acetic acid, formic acid and natural wax from the effluent (Buzzard, 1994).

A practical solution for effluent treatment would also increase the viability of a second FF plant. The furfural plant at Sezela adds value to bagasse, which is typically a low value stream used for fuel. The bagasse is rather reacted to make FF and then the bagasse residue is burned in the boilers. Overall, Sezela is required to burn coal to generate the required steam for the complex, but the coal cost is covered by the product revenue. Not only is furfural produced, but other organic chemicals such as furfuryl alcohol, diacetyl, 2,3-pentanedione and methanol are produced in small associated plants. Constructing a FF plant at a site with surplus bagasse in order to add value is therefore a real possibility. However, the most significant hurdle is the challenge of what to do with the effluent – it is unlikely that any site for a second FF plant would have a point available where it would be permitted to discharge untreated effluent. Economical effluent treatment is therefore a prerequisite for a second FF plant.

A unique challenge in treating Sezela's effluent is that it contains an unidentified toxin. When first attempting to treat the effluent in the 1980s, it was found that something present in the effluent inhibited biological growth. In later work it was found that microorganisms thrived on a synthetic Sezela effluent, but battled to survive on fresh effluent. Work has been done in an attempt to isolate and identify this unknown toxin, but without much success. It is believed that it occurs naturally in cane as protection against bacterial attack. More recent experience

has found that extended aeration of the effluent reduces its toxicity to microorganisms, with the retention time (at least a week) and the amount of aeration being the key factors (Robson, 2004). Nevertheless, the unknown toxin presents a hurdle to biological treatment processes, particularly the more sensitive anaerobic processes.

Previous attempts at treating the FF plant effluent

The FF plant at Sezela was commissioned in 1972 and the treatment of its effluent was first considered around 1980. Over the years many options have been considered, with most of them being tested at laboratory scale. A summary of the numerous options is given in Table 2. The treatment attempts were aimed at recovering the acetic acid as a product, or recovering the water to improve Sezela's water balance.

Table 2. Summary of previous attempts at treating furfural (FF) plant effluent.

Type	Treatment	Advantages	Disadvantages
Anaerobic	Anaerobic digestion ultrafiltration (ADUF)		Low loading rates
	Upflow anaerobic sludge blanket (UASB)	High rate process	Poor solids retention; low loading rates
	Lagoon		Large land requirements
Aerobic	Conventional activated sludge (CAS)	Proven technology	Expensive; large land use
	Single cell protein (SCP)	Value addition	Operational issues
Oxidation	Ozone/H ₂ O ₂ with UV light		Oxidation products
Adsorption			Large amount of resin required; desorption difficult
Acid recovery	Solvent extraction with alamine	Possibly financially feasible	Toxic solvent; operational issues
	Solvent extraction with ethyl acetate	Technically feasible	Energy intensive; not financially feasible
	Evaporation or distillation	Technically feasible	Energy intensive; not financially feasible
	Reverse osmosis/ membranes		Poor recovery; operational issues
	Neutralisation to form salts	Technically feasible	Not financially feasible
Irrigation			Low nutrient content; difficult to implement

It is possible to treat the FF plant effluent using aerobic or anaerobic biological processes. The two biological systems have very different characteristics (compared in Table 3), although certain considerations are common to both systems. Generally, in a mixed culture, certain microorganisms break down complex organic chemicals into simple carboxylic acids. Other microorganisms then consume the simple acids and produce carbon dioxide and other waste. The FF plant effluent has the advantage that simple acids (acetic, formic) are already available for microorganisms. However, it is devoid of the nutrients necessary for biological growth, mainly nitrogen, phosphorus and potassium (NPK). Therefore any treatment by

biological processes would require the addition of these nutrients, thus increasing the cost. The pH of the effluent also poses a problem as most microorganisms cannot survive in such an acidic environment. Neutralising the acetic acid before treatment is an option but requires very large amounts of chemicals. However, if the effluent is fed slowly enough, the consumption of the acid results in an acceptable pH.

Table 3. Comparison of aerobic and anaerobic processes.

Aerobic processes	Anaerobic processes
With oxygen	Without oxygen
Carbon in food released mainly as CO ₂	Carbon in food released mainly as CH ₄
Large amounts of sludge (biomass) produced	Much lower sludge production
Energy intensive (aeration)	Energy recovery possible (biogas)
Fast growing, stable	Very slow growing, sensitive
Suitable for low strength (low COD) effluents, 95% COD removal	Suitable for high strength effluents, 80% COD removal (normally need an aerobic polishing stage to achieve desired final effluent quality)

Anaerobic processes are preferred due to the low sludge production and the opportunity for energy recovery. Literature reviews were done for a number of anaerobic processes, and trials were done for the ADUF and UASB processes. The ADUF trial was a simple container without oxygen into which the effluent was fed. Membranes were used to withdraw the treated water and retain the solids (biomass) in the system (Membratek, 1991). UASB uses a similar digester but the biomass retention is by the process of biomass granules forming and settling. These granules form a blanket through which the effluent flows up. However, results from these trials were disappointing. After months of carefully conditioning the anaerobic bacteria (a typical start-up period for anaerobic plants), it was still found that the biomass could handle only very low rates of effluent. At high loading rates, the biomass would often die (Rosie, 1991). The very low feed rate achievable would have required unreasonably large digesters to treat the full effluent flow. When the unknown toxin was discovered a few years later, it was realised that this contributed to the difficulties with anaerobic processes.

An unavoidable hurdle to using anaerobic processes is that the effluent from the FF plant is seasonal. It is only generated for a maximum of nine months per year. During offcrop there would be no option but to let the anaerobic culture degrade. Upon start-up in the next season, at least a month would be required to recondition the microorganisms to the effluent. During this time, the process would be unable to handle the full FF plant effluent. Any treated water from the process would also be of poor quality. Thus using an anaerobic process would unfortunately require provision for the discharge of untreated effluent for at least the first month of every season.

Both aerobic and anaerobic processes have been used to treat effluents similar to the FF plant effluent. A byproduct of both Sasol and PetroSA's processes to produce liquid fuels is an aqueous stream with low concentrations of simple organic acids. Sasol's reaction water is treated by very large aerobic plants that are energy intensive and require large amounts of land. PetroSA's effluent is treated anaerobically in downflow stationary fixed film (DSFF) reactors. Recently they have invested in gas engines to recover energy from the biogas generated in the digesters. Sasol is also planning on installing anaerobic digesters similar in

design to those of PetroSA (SSI Environmental, 2008). Unfortunately, treating Sezela's effluent using this anaerobic process is not feasible due to the unknown toxin present. Also, the petroleum effluents are generated all year round. Using the aerobic conventional activated sludge (CAS) treatment would be incredibly expensive and is unreasonable for Sezela.

An aerobic process that did show some promise was to use the effluent to grow mycoprotein, or single cell protein (SCP). This is a similar process to CAS except that, instead of the biomass being made up of numerous species of microorganisms (a mixed culture), one organism is allowed to dominate (a monoculture). This organism is then harvested in a concept similar to wasting excess activated sludge. The SCP process is patented, and in fact mycoprotein is produced and sold for human consumption in the USA and the European Union. It is a high protein, low fat food source similar to soybean or fishmeal (Marlow Foods Ltd. <http://www.quorn.com/About-Quorn/>). A small pilot plant treating less than 1m³/d of effluent was operated at Sezela. The protein that was produced underwent trials for use in animal feed, with encouraging results. An advantage of the process was that the conditions of the FF plant effluent were favourable to the growth of the specified fungus, making a monoculture easy to obtain without expensive equipment and practices. However, the expected growth rates could not be achieved. After a lengthy trial period, there were some aspects that still needed work, such as an internal recycle stream with sterilisation. However, the product was too far from Sezela's core business and, with a lot of work still to be done, the project was abandoned when the budget was exhausted.

Non-biological methods of treating the effluent have the advantage of being unaffected by the unknown toxin. For instance, the organic material in the effluent could be oxidised using hydrogen peroxide (H₂O₂) or ozone (O₃). However, the resulting oxidation products could be hazardous and the quality of the water, although free of COD, could still be poor. These oxidation methods have not been tested (Treffrey-Goatley, 1991). Another method considered was to use a resin to adsorb the organic material. However, it was found that desorption (regeneration of the resin) was poor. Also, prohibitively large amounts of resin would be required to treat the large volumes of effluent (Treffrey-Goatley, 1991).

Significant effort was invested in trying to recover the acetic (and formic) acid from the effluent. Solvent extraction showed the most promise and a few different solvents were tried (Somera, 2002). However, extracting the acid does not solve the effluent problem as the large amounts of remaining water still needed to be treated. Also, the acetic acid concentration in the effluent was too low to make its recovery financially feasible. It was estimated that the lowest concentration to make the recovery of acid economically viable was 4 wt%. It was suggested that the acid in the effluent be concentrated by evaporation or distillation, but generally this was not financially feasible, amongst other concerns (Traicos, 1993).

Using the effluent to irrigate the surrounding cane fields was also considered. However the effluent has very little nutritional value and the topography of the fields surrounding Sezela does not lend itself easily to irrigation.

Review of the membrane bioreactor (MBR)

A technology that has been found in recent years to be successful in treating FF plant effluent is the membrane bioreactor (MBR). Sezela's MBR is a large open tank (4000 m³) filled with effluent through which air is bubbled by diffusers along the bottom of the tank. There is a bank of flat sheet membranes submerged in the tank through which the clear permeate passes

(Figure 2). It was constructed as a 'pilot' plant and was designed to treat a third of the effluent from the FF plant. It has been in operation since 2005, and much has been learned since then both about its operation and the characteristics of the effluent. Practically, it has been found that it can satisfactorily treat 25% of the FF plant effluent.

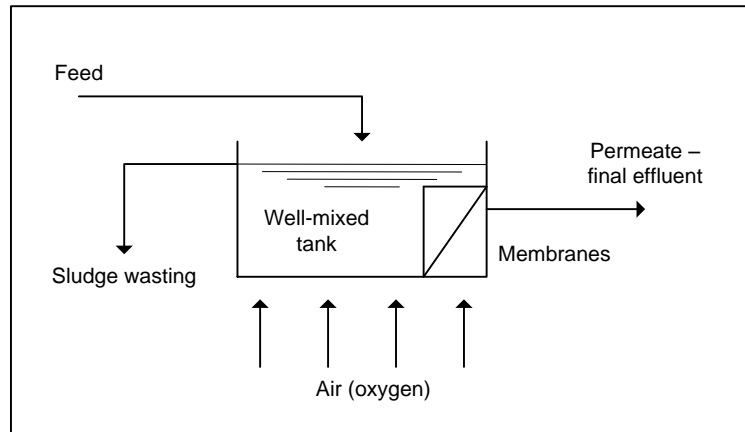


Figure 2. Simplified diagram of the membrane bioreactor (MBR).

Two large blowers supply air via fine bubble diffusers along the floor of the tank. A third smaller blower supplies air as coarse bubbles used to scour and clean the membranes (in all membrane operations regular cleaning is necessary to prevent fouling the membranes). The plant is operated by controlling a number of parameters such as tank pH, dissolved oxygen and MLSS. Sludge is wasted from the tank to maintain MLSS in the range of 12 000 to 14 000 mg/L. Nutrients of nitrogen and phosphorus (as urea and phosphoric acid) are added for healthy biological growth. These are dosed manually to ensure a residual amount of N and P in the permeate. When operating in a stable manner, the MBR easily achieves 95% COD reduction and is capable of achieving a final effluent COD below 200 mg/L. An issue, however, is that the permeate colour remains high.

The temperature at which the MBR operates was unplanned. When the microorganisms are actively consuming the COD, the MBR temperature is consistently around 50°C. It was assumed that the plant would operate around 30°C and contain a microorganism population that was mesophilic. However, the FF plant effluent typically enters the MBR at 40°C, and, with the consumption of COD being exothermic, the temperature is raised to above 50°C. At these temperatures, the culture of biomass becomes thermophilic. Thermophilic populations have different characteristics to mesophilic ones. A notable advantage is that the thermophilic culture seems to result in much lower sludge production rates, with a larger proportion of organic material being converted to gaseous products. However, the disadvantage of the elevated operating temperature is that the reactor is unstable between 48°C and 50°C, as the culture fluctuates between mesophilic and thermophilic (Kennedy and Young, 2007). This instability is compounded by the effluent feed being inconsistent, depending on the operation of the FF plant.

The key to the success of the MBR at Sezela is that its use of membranes allows a higher biomass concentration. This technology has only recently become available because of the progress in membrane technology, which has resulted in cheaper and more robust membranes. In the MBR, the membranes efficiently separate the solids out to allow a clear final effluent. The membranes operate in the ultrafiltration range, having a pore size of 0.1-

0.4 μm (Fitzgerald, 2005). Conventional aerobic plants rely on clarifiers to separate the solids from the final effluent. Thus, to achieve a suitable effluent quality, the MLSS in the sludge reactor is limited. However, the MBR at Sezela can still produce a reasonable permeate with MLSS concentrations over 25 000 mg/L. A high concentration of biomass is more resilient to the unknown toxin present in the effluent – if some of the biomass dies in consuming the toxin, there is still sufficient biomass to treat the COD in the effluent.

To treat the full effluent load from the FF plant, an additional three MBRs would be required. Although the MBR has been proven capable of treating the FF plant effluent, it has major shortcomings, namely its unreliability and high electricity cost. As mentioned above, there is instability due to the temperature operating range. There have also been occasions when the biomass population in the MBR unexpectedly stops consuming the acid. The effluent feed to the plant needs to be virtually stopped to allow the plant to recover, which can take as long as a week. This unreliability would necessitate a fifth, spare MBR to be installed in a full scale plant, to provide back-up capacity. The process, being aerobic, also has large power requirements. The electricity cost of the MBR was assessed by Robson (2009). The MBR consumes approximately 635 kW when operating at maximum. When commissioned in 2005, the energy costs were about R650 000 p.a. However, the price of electricity has risen drastically since then. Robson (2009) estimated that the electricity cost of a MBR treatment plant large enough to treat the entire FF plant effluent would be R9 million in 2012. The effluent treatment alone would therefore amount to R450/ton FF. This would have a serious effect on the economics of constructing a second FF plant.

Application of MBR technology in sugar mill context

MBR technology has become established in parts of the world, particularly in treating municipal effluents. This is mainly due to its compact, self-contained nature as well as its high quality treated effluent, which makes it suitable for re-use. Of particular interest in municipal applications, the ultrafiltration membranes also screen out most viruses and pathogens, eliminating the need for sterilisation of the final effluent (AMTA, 2007). The ability of the MBR to operate with a higher MLSS than conventional activated sludge plants allows the reactor volume to be reduced while achieving the same loading rate. It also requires less infrastructure than a conventional plant as a single tank performs most of the processing. The MBR therefore requires much less land and can be cheaper to construct.

At Sezela, a rough comparison can be made between the MBR and the conventional activated sludge plant. A direct comparison cannot be drawn as the two plants were designed to treat completely different effluents. However, Table 4 gives an indication of the capabilities of the two plants. The figures reported are averages taken over the previous three years (2009 to 2011). It should be noted that the conventional plant is currently operated in excess of its design capacity, and so its poor performance is to be expected. The figures given for the MBR are an average over its full operating period, including times of instability when its capacity is reduced. When running in a stable manner, the achievable hydraulic and COD loads are appreciably higher than the average figures given in Table 4.

It is immediately apparent that the MBR has one quarter the footprint of the conventional plant, with almost five times the COD treatment capacity. To illustrate this difference, Figure 3 shows an aerial view of Sezela's effluent treatment plants. The MBR is the circular tank on the far right; the conventional plant consists of the two rectangular tanks in series and the circular clarifier along the top of the photo. The conventional plant also includes

extensive underground piping connecting the three tanks and ancillary equipment. It is clear that the MBR is a simpler, smaller installation.

Table 4. Comparison of performance of the two effluent treatment plants at Sezela.

		Conventional plant	MBR
Land usage	m ²	2460	640
Volume	m ³	5300	3970
Hydraulic load	m ³ /d	1200 (design); 1680 (actual)	1200 (design); 550 (actual)
COD load	kg/d	3300 (design); 5330 (actual)	15 000 (design); 9350 (actual)
Inlet COD	mg/L	3140	17 000
Outlet COD	mg/L	1020	850
COD reduction		70%	95%
MLSS	mg/L	6600	12 500
Sludge wasted	m ³ /d	125	80
Power requirements	kW	255	635



Figure 3. Aerial view of the effluent treatment plants at Sezela.

The MBR has successfully been run during offcrop on a feed of domestic effluent and offcrop washings. It has been seen to perform well, achieving better final effluent results than the conventional plant. The MBR could therefore suitably replace and fulfil the duty of the conventional plant. The inclusion of domestic effluent from the surrounding residential area also brings nutrients, decreasing the amount of nutrient addition required. A disadvantage is that this effluent feed contains a greater amount of dissolved salts, which foul the membranes more quickly. As a result, more regular chemical cleans are required when operating in this mode.

A major advantage of the MBR is that it produces a good quality final effluent. However, sugar mills do not often have serious demand for water re-use. Re-using the permeate for imbibition has been considered (Robson, 2007). The MBR is also capable of handling higher

strength effluents. From experience at Sezela, the conventional plant can be very difficult to operate when slug loads of sugar are present in the effluent, such as when there are spills. The instability of Sezela's MBR has been noted above. However, this instability is directly related to the acidic nature of the effluent, and the reactor's elevated operating temperature as a result of the hot, high COD feed. An MBR operating on sugar mill and domestic effluent should not experience this instability.

Other experience with an operating MBR is that a screen upstream is essential. The membranes do not handle stringy material well, including bagasse fibres. The incoming effluent may require multiple stages of screening. A recommendation is that final screen size should be smaller than 2 mm (AMTA, 2007). At Sezela a DSM screen is used, identical to that used to screen draft juice in a cane diffuser.

Generally, the maintenance on the MBR is minimal. Occasional chemical cleans are required on the membranes (once every few months), and membrane life is expected to be about 10 years. It has been found that the diffused aeration system needs to be inspected every year or so, and repaired if necessary. Additional maintenance includes servicing the blowers and pumps.

At a green-field installation, if there was a shortage of space and a shortage of water, an MBR would be highly suited as the effluent treatment solution, as it is compact and gives high quality water suitable for re-use.

Conclusions

The FF plant effluent is difficult to treat, with the unknown toxin being a unique challenge for biological treatment. However, treatment is necessary to prevent discharge to sea. This will ensure the continued operation of Sezela's FF plant and make the construction of a second FF plant feasible. Although many different attempts have been made at treating the effluent, none have presented a practical solution. Opportunities exist in the recovery of water to improve Sezela's water balance, or in the recovery of acetic acid and other products from the effluent.

The MBR has proved that it is capable of successfully treating the effluent. However, due to the high power costs inherent in the aerobic process, it is not financially feasible as a full scale effluent treatment solution. Some surprising aspects are that it operates thermophilically and with very low sludge production.

The MBR at Sezela has also been operated satisfactorily on a combination of sugar mill and domestic effluent. It could be considered as a solution to effluent treatment at sugar mills. However, it would only have significant advantages over conventional activated sludge plants if there were space limitations and water re-use was a priority, both of which are uncommon in the sugar industry.

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