

TREATMENT OF HIGH STRENGTH CHEMICAL INDUSTRY WASTEWATER USING MOVING BED BIOFILM REACTOR (MBBR) AND POWDERED ACTIVATED CARBON (PAC) TECHNOLOGY

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ABSTRACT

A new Waste Recycling Facility (WRF) was created at the Sasol coal to liquids facility in Secunda, South Africa with a wastewater treatment system that includes equipment to treat the wastewater and storm water through several steps including equalization, oil removal (gravity separation and dissolved air flotation), lime neutralization/metals precipitation, back-neutralization, fixed-film biological treatment, powdered carbon activated sludge biological treatment, sand filtration and chemical oxidation. It is a unique facility believed to be a first of kind. A pilot study was performed on the fixed film biological treatment unit using the AnoxKaldnes Moving Bed Biofilm Reactor (MBBR) technology for pre-treatment of the wastewater followed by powdered activated carbon (PAC) for additional removal of organic material & nitrification. The start up of the MBBR system was in August 2005 and the waste recycling facility has met beneficial operations since December 2005.

KEYWORDS

Biological treatment, chemical wastewater, moving bed biofilm reactors, powdered activated carbon

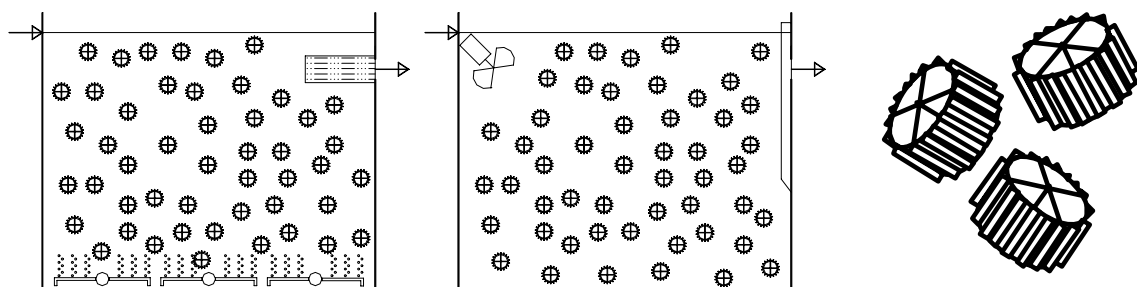
INTRODUCTION

The Sasol's coal to liquids complex located in Secunda, South Africa uses processes based on gasification of coal using Lurgi technology and the Sasol Advanced Synthol Fischer-Tropsch Reactors. Wastewaters at the facility are derived from various oily and organic wastes generated in facility unit operations. A new unique Waste Recycling Facility was created with a wastewater treatment system that includes equipment to treat the wastewater and storm water through several steps including equalization, oil removal (gravity separation and dissolved air flotation), lime neutralization/metals precipitation, back-neutralization, fixed-film biological treatment, powdered carbon activated sludge biological treatment, sand filtration and chemical oxidation. The combination of technologies is novel and offers maximum flexibility which enables treatment of effluents highly polluted with organic material.

A pilot study was performed on the fixed film biological treatment unit using the AnoxKaldnes Moving Bed Biofilm Reactor (MBBR) technology for pre-treatment of the wastewater. The pilot study was conducted over a 5 month period of time after which showed how well the system removed greater than 90% of the soluble COD. After the MBBR was proved as a viable pre-treatment technology, a continuous pilot study on a powdered activated carbon activated sludge system treating the effluent from the MBBR was performed to monitor the overall COD removal and nitrification.

MOVING BED BIOFILM REACTORS

This process is based on a continuously operating, non-clogging biofilm reactor with no need for backwashing, low head loss and a high specific biofilm surface area. This is achieved by having the biofilm (or biomass) grow on both small carrier elements that move along with the water in the reactor (attached growth) as well as in the water itself (suspended growth). The movement within the aerobic reactor is generated by the aeration energy (see Figure 1a). Mixing of carrier elements under anoxic conditions (denitrification) is provided by slow speed mixers (see Figure 1b). The biofilm carrier elements are made of polyethylene, having a density slightly less than water, and are shaped like small cylinders (about 10 mm in diameter and 7 mm height) with a cross inside the cylinder and longitudinal fins on the outside (see Figure 1c). To keep the carrier elements inside the reactor a sieve assembly with approximately 5 mm openings are placed on the influent and effluent ports of the reactor. The agitation in the reactor is so arranged that the carrier elements are constantly being moved upwards over the surface of the sieve. This action creates a scrubbing effect that prevents clogging.



a. Aerobic reactor b. Anoxic and anaerobic reactor c. The biofilm carrier (K1)

Figure 1 - MBBR™ biofilm technology principle and shape of the original biofilm carrier (K1)

The filling of carrier elements in the reactor may be decided for each case, giving considerable flexibility in the specific biofilm surface area. A maximum filling of about 70%, based on empty reactor volume corresponds to a specific growth area of biofilm of about $350 \text{ m}^2/\text{m}^3$. The reactor volume is totally mixed and consequently there is no dead or unused space in the reactor.

Different reactor shapes can be used and the MBBR process is ideal for upgrading of overloaded activated sludge plants or for converting unused tankage into biofilm reactors. Figure 2 shows the actual aeration system and screen assembly used for this system.

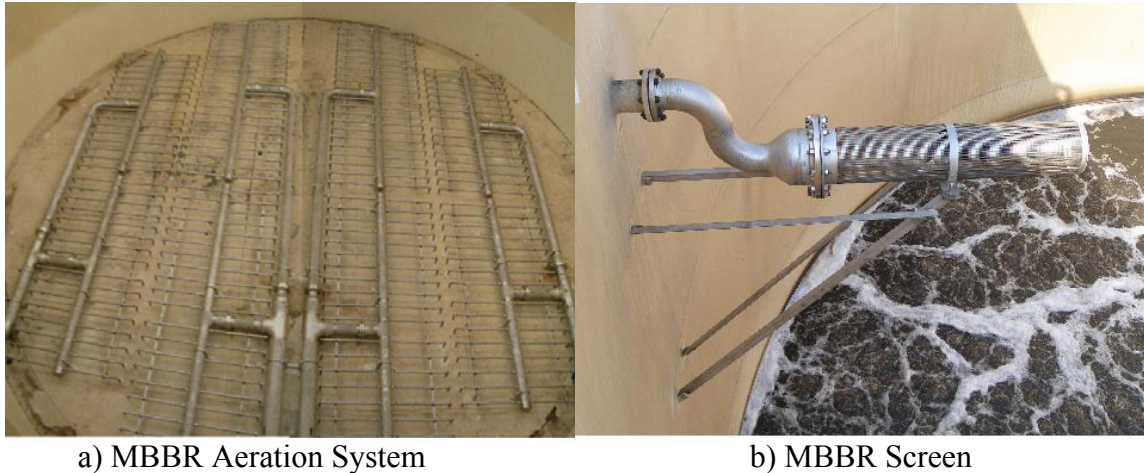


Figure 2 – MBBR System Components

THE SASOL WASTE RECYCLING FACILITY

The Sasol WRF complex has been designed to treat wastewater generated from a small wastewater stream on site. The design flow for the system is 145,000 gpd (23 m³/hr) and the overall design of WRF is to purify the incoming wastewater in a series of steps to produce cooling water make-up use in the plant (see Figure 3 & 4). The first step in this process is removal of oils via an API separator & Dissolved Air Flotation (DAF) system. The clarified effluent from the Chemical Treatment is then pH adjusted (if necessary) prior to entering the MBBR Fixed Film Bio-Reactor. Nutrients are added (if necessary) in the MBBR. As the wastewater also has phenols and ammonia which need to be removed, the next step in the process helps reduce these items in the powdered activated carbon activated sludge system which incorporates a single reactor and secondary clarifier. Clarified effluent flows to a holding tank where effluent from this is fed to sand filters prior to being sent to a chemical oxidation unit using ozone or hydrogen peroxide. Final treated effluent from the chemical oxidation unit is then re-used as make up water to the cooling tower. A large portion of this treated water is used in the WRF internally. Waste activated sludge is sent from the secondary clarifier to a sludge thickener prior to be sending to a plate and frame filter press.

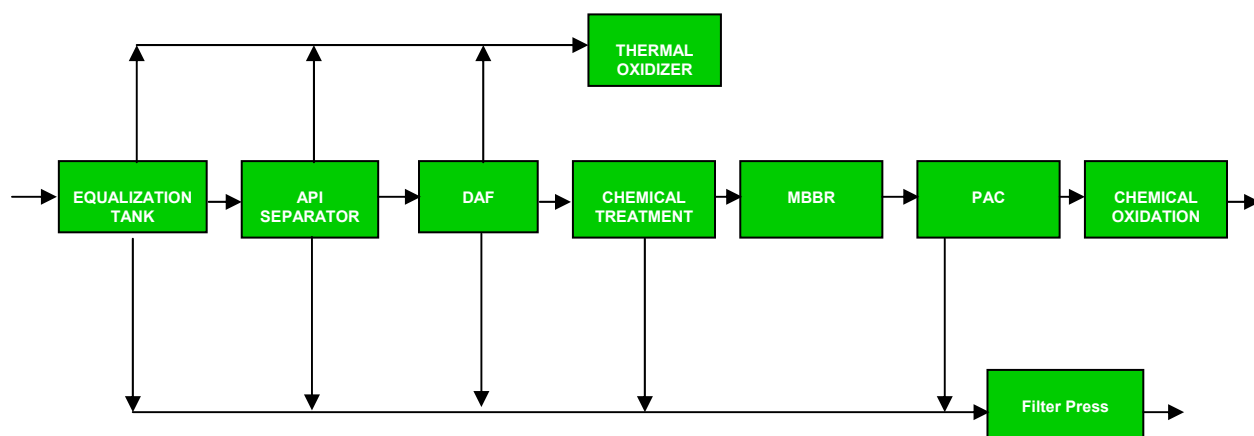


Figure 3 – Sasol WRF Flow Diagram

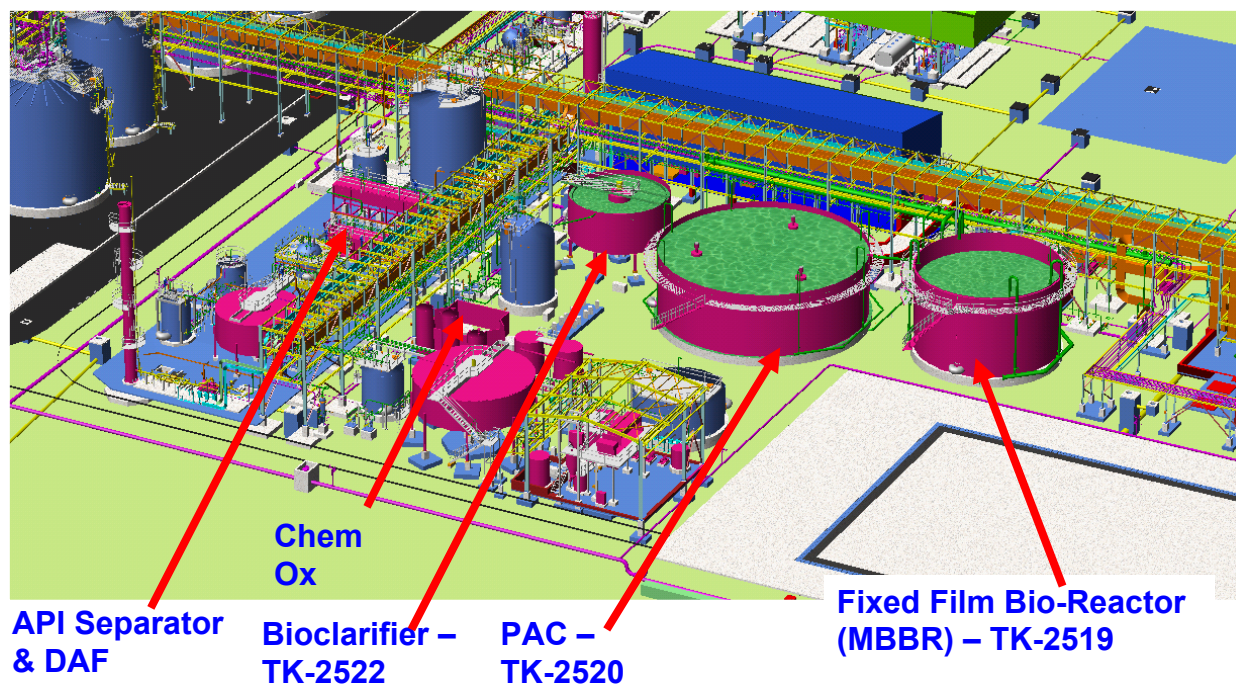


Figure 4 – Sasol WRF Layout

PILOT STUDY DESCRIPTION & RESULTS

The MBBR pilot test was performed in two bench scale AnoxKaldnes MBBR's (R1 and R2), Figure 5. The bench scale reactors were made of glass and had a volume of 0.264 gallons (1 liter) each. Both reactors contained AnoxKaldnes K1 carrier material, which has an effective surface area for biofilm growth of $152.4 \text{ ft}^2/\text{ft}^3$ ($500 \text{ m}^2/\text{m}^3$) at 100 % filling. The filling degree of carriers was 38% in Reactor 1 and 46 % in Reactor 2, corresponding to an area for biofilm growth of $57.9 \text{ ft}^2/\text{ft}^3$ ($190 \text{ m}^2/\text{m}^3$) in R1 and $70.1 \text{ ft}^2/\text{ft}^3$ ($230 \text{ m}^2/\text{m}^3$) in R2. The influent wastewater feeds were pumped continuously with a multi-channel peristaltic pump. Most of the time, the feed rate was set at approximately 0.114 gpd (430 mL/day) in R1 and 0.137 gpd (520 mL/day) in R2, corresponding to hydraulic retention times of approximately 56 hours in R1 and 46 hours in R2.

The temperature of each reactor was controlled by circulation of water from a thermostat bath through the jackets of the reactors. The pH in the reactors was kept around 7 by adding sodium hydroxide to the feeds. Phosphate (KH_2PO_4) was also added to the feeds to avoid nutrient deficiency. The reactors were aerated in order to provide oxygen for the degradation and to keep the carriers in constant movement. The incoming air was humidified in order to avoid uncontrolled evaporation from the reactors. In spite of this, the evaporation from the reactors was approximately 15 %.

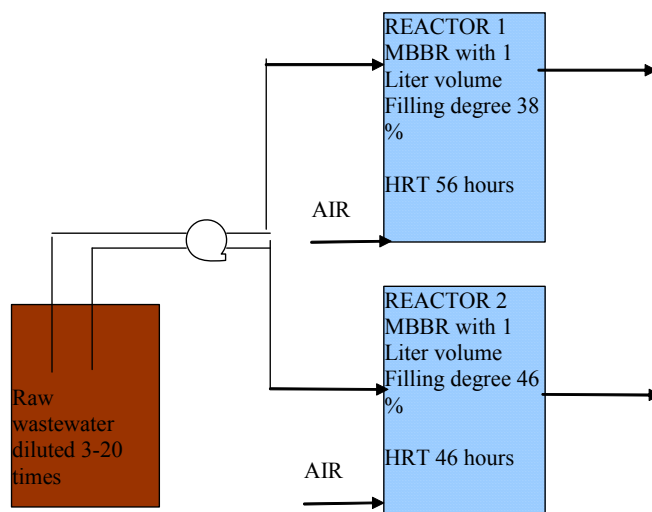


Figure 5 – MBBR Pilot Study Flow Diagram

The wastewater sample used in the study was produced by Sasol and arrived at the AnoxKaldnes testing laboratory in three drums. The contents of the drums were mixed in order to obtain one uniform sample, which was then divided into 25-liter plastic containers. The containers were stored at 2-5 °C.

Results from analyses on the uniform wastewater sample, before biological treatment is shown in Table 1.

Parameter	Filtered sample	Non-filtered sample
COD (mg/l)	57,000 (56,000)	57,500
BOD5 (mg/l)	38,850	39,900
TOC (mg/l)	16,930	16,630
IC (mg/l)	32	34
Phenols (distillable) (mg/l)	5,000 (6,000)*	
Cyanide (total) (mg/l)	13 (60)	
Cyanide (free) (mg/l)	5.8	
N-tot Devardas (mg/l)	3,855 (3,700)*	3,870
NH4-N(mg/l)	2,955 (3,100)*	
NO3+NO2-N(mg/l)	0.07	
P-tot (mg/l)	<5	<5
PO4-P(mg/l)	0.12	
Sulfate (mg/l)		9,600
Sulfide (mg/l)		0.78
TDS (mg/L)	16,800	
TSS (mg/l)		196
VSS (mg/l)		104
pH		8.8

Table 1. Pilot study wastewater sample analyses

Results from the pilot study showed that an influent containing nearly 20,000 mg/L COD could be treated by biodegrading over 90% of its soluble COD and phenols in the MBBR. Figure 6 below shows the influent phenol concentration to the two (2) bench scale units which ranged between 1,200 & 1,600 mg/L and were degraded to less than 15 mg/L on a consistent basis. Performance of the MBBR was shown to relate to the phenol effluent concentration, i.e., when the residual phenol increased, the overall organic reduction of the MBBR decreased.

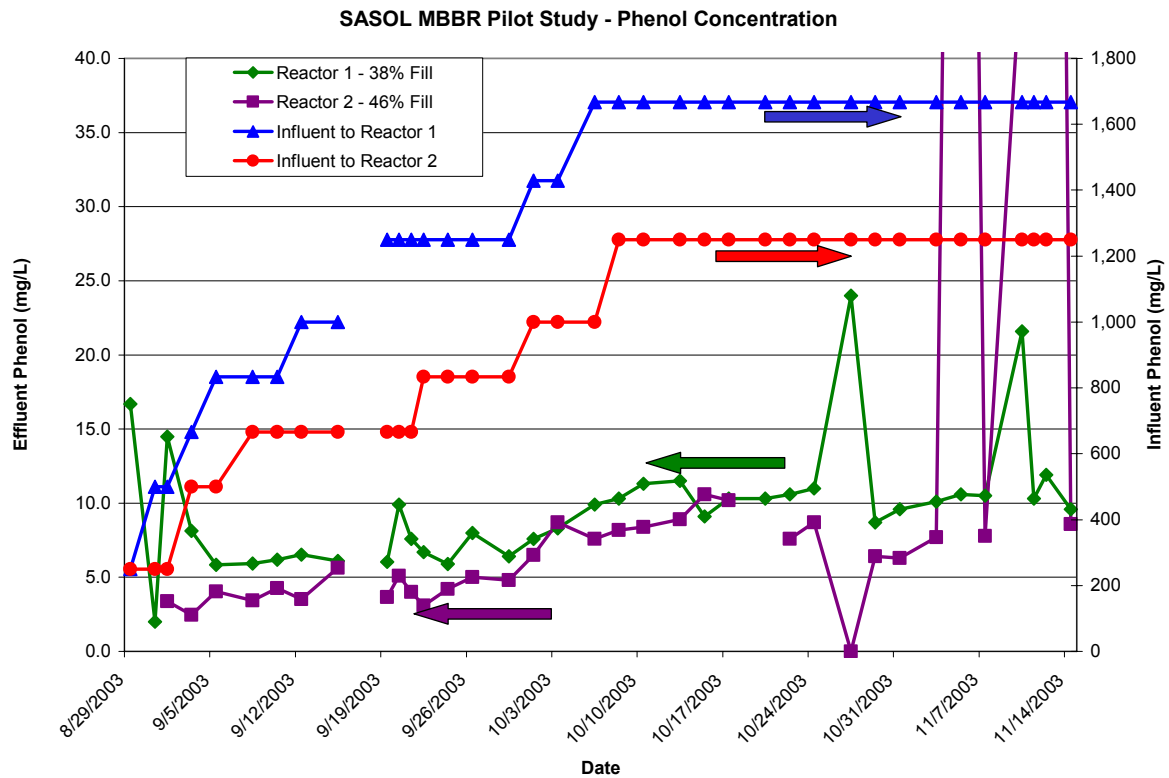


Figure 6 – Pilot Study MBBR Phenol Concentration Profile

Plotting the COD profile similar to that of phenol shows how the influent concentration started out at near 3,000 mg/L by increasing the dilution of wastewater to dilution water. As the system was capable of meeting effluent concentrations less than 1,000 mg/L (and maintained the steady effluent phenol concentrations) the wastewater dilution factor was steadily decreased. The changes in the dilution allowed the influent concentrations of soluble COD to steadily increase in a step wise fashion to the target concentrations of 14,000 and 19,000 mg/L. The overall timeline from the start of the pilot to full system concentration was 2 months. During the entire pilot study the MBBR was meeting less than 1,500 mg/L of soluble COD showing an overall removal of greater than 90%.

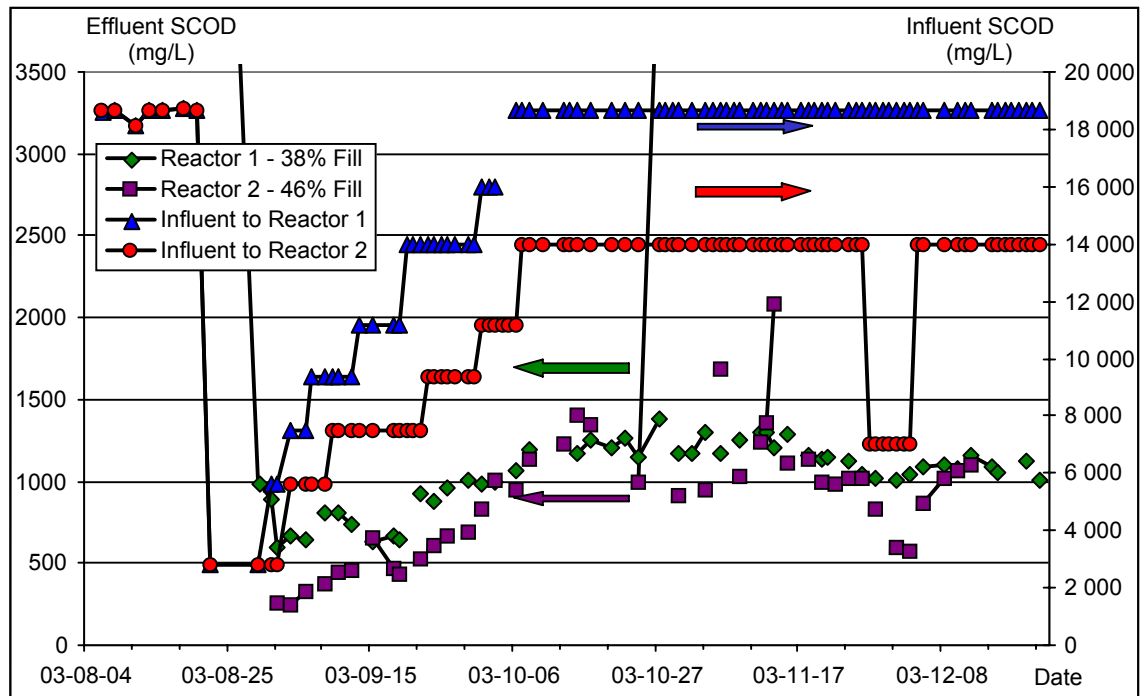


Figure 7 – Pilot Study MBBR COD Influent Concentration vs. Effluent Concentration

As the MBBR has the media in the reactor, the evaluation of performance of the MBBR is based on the surface area provided for biofilm growth. All MBBR systems are designed and analyzed on the value described as the surface area loading rate (SALR). The SALR is represented as load per surface area – time ($\text{g COD/m}^2\text{-day}$) and the removal efficiency is described as the removal rate (RR). Figure 8 shows the overall surface area loading rate vs. removal rate during the pilot study for both Reactor 1 and Reactor 2 for soluble COD and the graphic shows that across a wide range of loadings ($10 - 50 \text{ g COD/m}^2\text{-day}$), the removal was consistently greater than 90%.

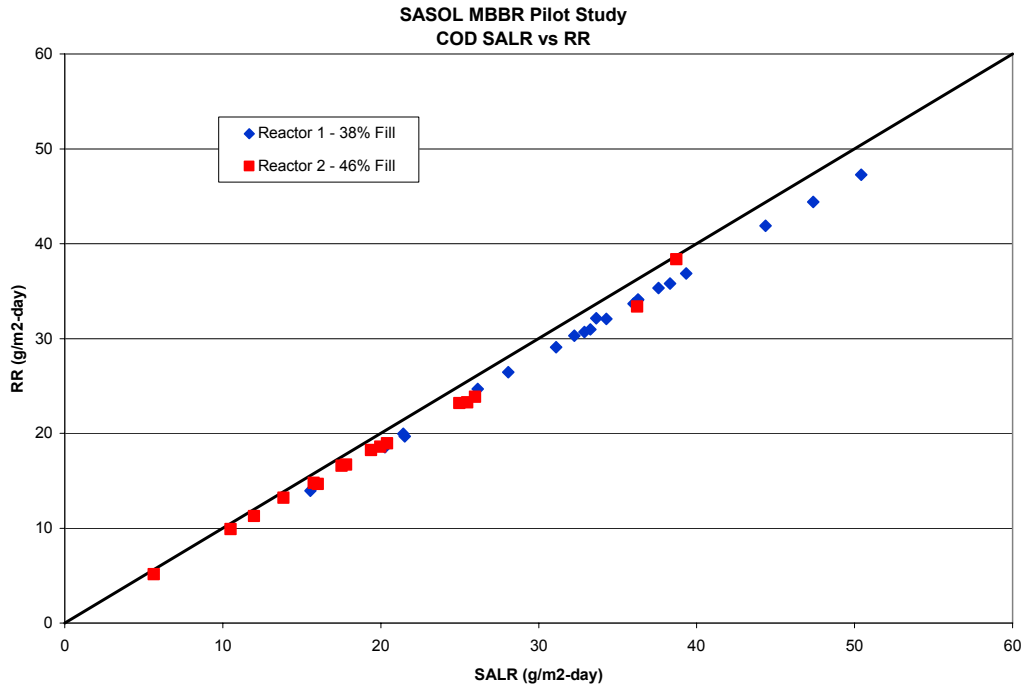


Figure 8 – Pilot Study MBBR COD Surface Area Loading Rate vs. Removal Rate

Once the pilot study demonstrated the ability to pre-treat the wastewater, a bench scale Powdered Activated Carbon (PAC) system was placed down stream of the MBBR for further reduction of the organic material, nitrification of the relatively high (nearly 500 mg/l) ammonia concentrations contained in the wastewater, and adsorption of recycled recalcitrant compounds. Figure 9 shows the COD reduction across the Powdered Activated Carbon system down to less than 600 mg/L achieving the targets set out by the system. Residual BOD values approached insignificant levels.

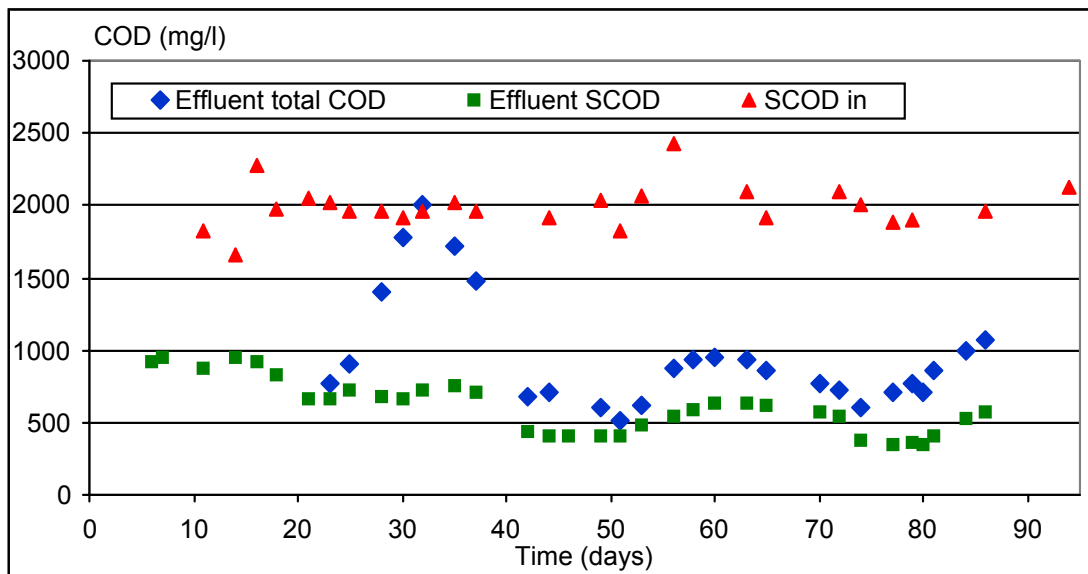


Figure 9 – Pilot Study Powdered Activated Carbon System COD Profile

Figure 10 shows the effluent profiles for ammonia, nitrate and nitrite over time for the PAC System and shows the ability of the system to completely nitrify the ammonia contained in the wastewater. After successfully demonstrating the MBBR + PAC system combination was able to treat the overall wastewater to the effluent limits set, a full scale system was constructed.

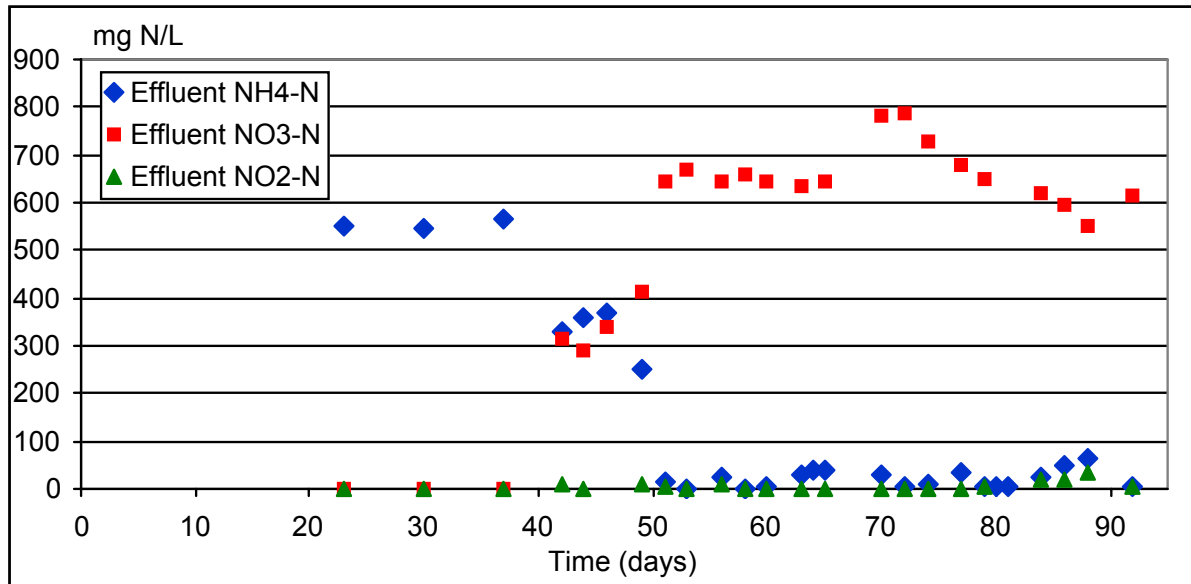


Figure 10 – Pilot Study Nitrification in PAC System over time

FULL SCALE PLANT DESIGN

The positive results from the pilot study confirmed the treatability of the wastewater and a full scale design was generated. The Sasol WRF placed the AnoxKaldnes MBBR treatment system into a single reactor on site which was ahead of the powdered activated carbon activated sludge reactor system. Specific design criteria and a flow diagram of the treatment facility are shown in Table 2 – Kaldnes MBBR Design Specifications and Figure 9 – Full Scale Flow Diagram, respectively.

Design Average Flow (MGD)	0.145
Design Soluble BOD Load (lb/day)	12,770
Design Soluble COD Load (lb/day)	18,242
Design Max. Temperature (°F)	104
Diameter (ft)	50
Water depth (ft)	23
Wet volume (ft ³)	41,524
Specific biofilm surface area (ft ² /ft ³)	60.96
Bulk volumetric filling of carriers (%)	40
Hydraulic Retention Time at Design Flow (hours)	51

Table 2. AnoxKaldnes MBBR Design Specifications

The full scale MBBR system was brought on line in August 2005 with the PAC system following in December 2005. Figure 11 shows an aerial view of the complete biological treatment system showing the MBBR at the top of the picture which flows via gravity into the PAC tank which then flows via gravity to the secondary clarifier.

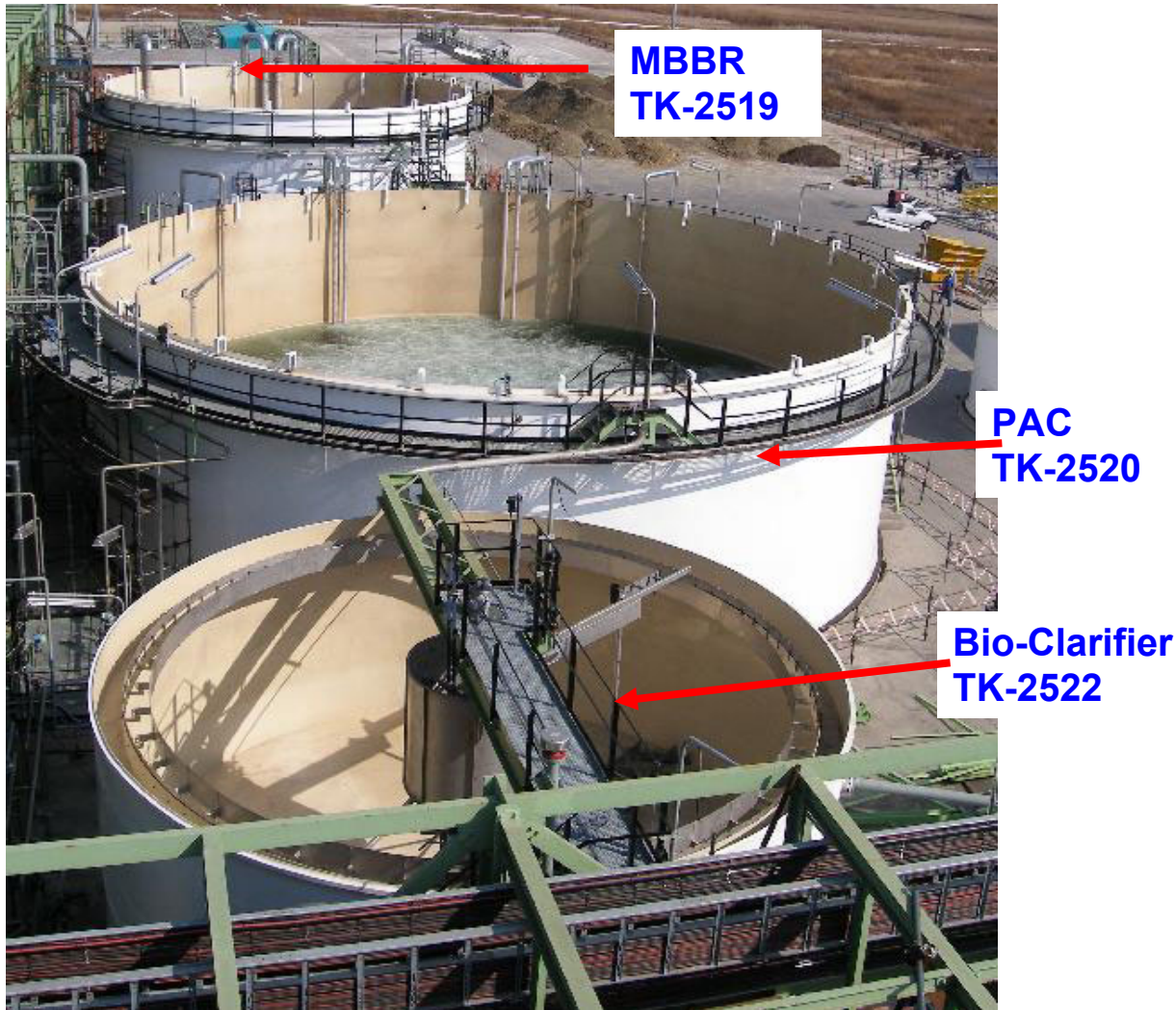


Figure 11 – Aerial shot of Sasol WRF Biological System

The full scale MBBR system was brought on line in August 2005. There were 467 bags of media loaded in to the MBBR. This represented approximately 450 millions pieces of media. An extended commissioning plan was created for the MBBR based upon the successful pilot plant operations. The MBBR commissioning was planned to achieve a performance test of 7.17 lb COD/1000 ft²-day (35 g COD/m²-day). The commissioning followed the plan and had a gradual growth of the biofilm on the media over a 90 day period of time. There were 15 steps in the commissioning plan. Table 3 show the goal of start up similar to the pilot study using a step system for increasing load with respect to the period in time after start-up, SALR, Feed COD concentration and the feed flow rate.

Day	Period (days)	SALR (g COD/ m ² -d)	Feed COD (mg/L)	Feed Flow (MGD)
15-Sep	16	2.7	5,000	0.033
28-Sep	29	3.6	5,000	0.044
30-Sep	31	4.65	5,000	0.057
1-Oct	32	6.45	7,000	0.057
6-Oct	37	10	7,000	0.088
10-Oct	41	14.5	14,000	0.064
13-Oct	44	12.5	10,000	0.077
18-Oct	49	15.5	10,000	0.096
20-Oct	51	20	11,000	0.112
27-Oct	58	18.75	13,000	0.089
3-Nov	65	20.25	14,000	0.089
10-Nov	72	26.25	15,000	0.108
17-Nov	79	29.3	15,000	0.120
24-Nov	86	32.5	15,000	0.134
1-Dec	93	35	15,000	0.144

Table 3 – MBBR Commissioning Steps

The acclimation period saw constant COD removal from August to November where the SALR steadily increased up to 4.1 lb/1000 ft²-day (20 g COD/m²-day). The system had a minimum 80% COD Removal in the MBBR during the entire acclimatization period. Figures 12 shows the flow rate to the MBBR and PAC system over time and shows that since the MBBR was removing too much COD, a small bypass of raw wastewater to allow the PAC system to have some food.

Figure 13 is the COD profile feeding the MBBR and PAC system. In this graphic the influent wastewater to the MBBR was provided by PC-2503 & PC-2513. The average influent COD concentration to the MBBR over this period of time with all the fluctuations has been 9,366 mg/L with an effluent concentration out of the MBBR of 2,020 mg/L. With the by-pass of raw wastewater on and off during the first 9 months of operation the average influent COD concentration to the PAC system has been 2,893 mg/L the effluent COD from the secondary clarifier has been 1,042 mg/L.

Looking at the MBBR performance and converting the concentrations and flow rate with the reactor volume, Figure 14 shows the SALR vs. Time for the MBBR since start up. Due to lack of large volumes of wastewater at start up, the COD surface area loading rate has varied widely and after middle of November the system saw a large drop off in the waste load SALR. Even since January 2006 the overall SALR has been trending lower due to the overall lack of wastewater with the delay of the plant shutdown. The plant shutdown would have filled the WRF Tank farm and provided a large quantity of wastewater to be treated over an extended period of time. However, the lack of shutdown wastewater provided an opportunity for the WRF to successfully treat highly toxic waste streams that were not in the original design scope, showing the robustness and flexibility of the processes.

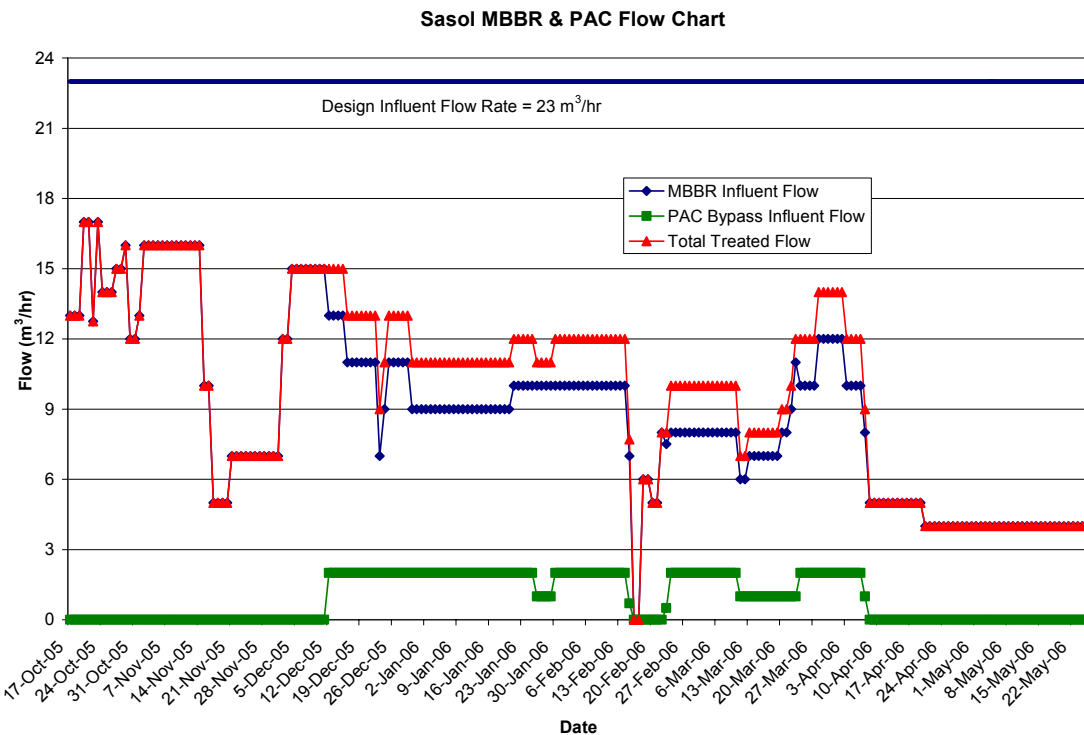


Figure 12 – Full Scale MBBR & PAC Flow Rates

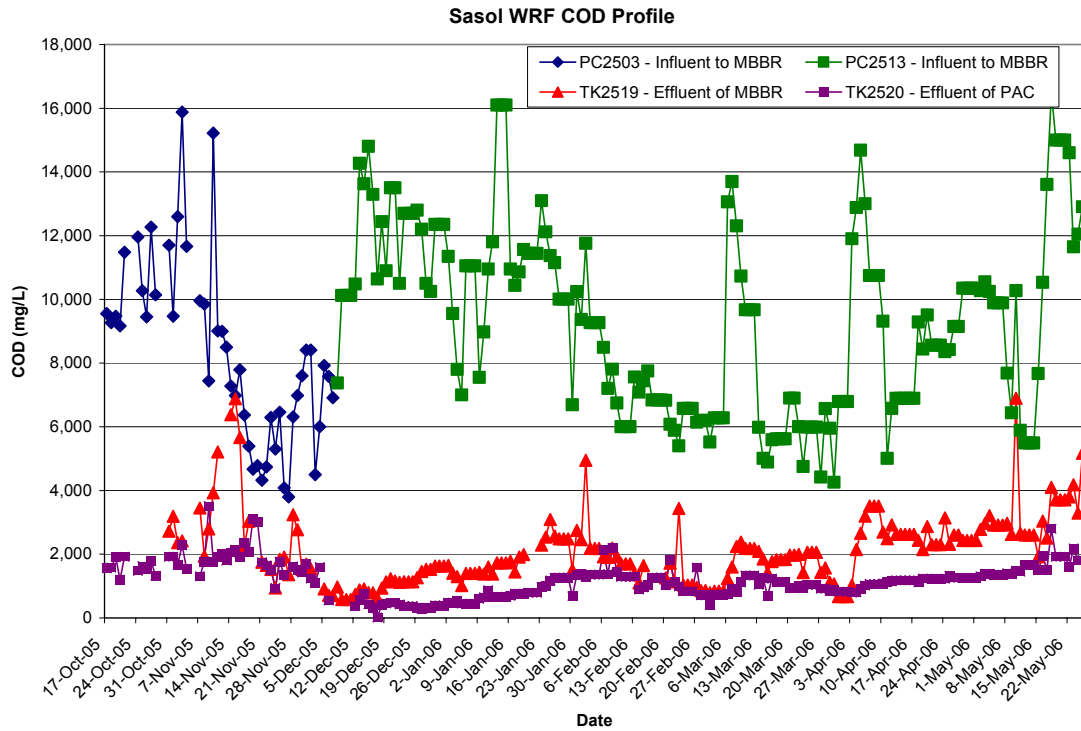


Figure 13 – Full Scale MBBR & PAC Flow Rates

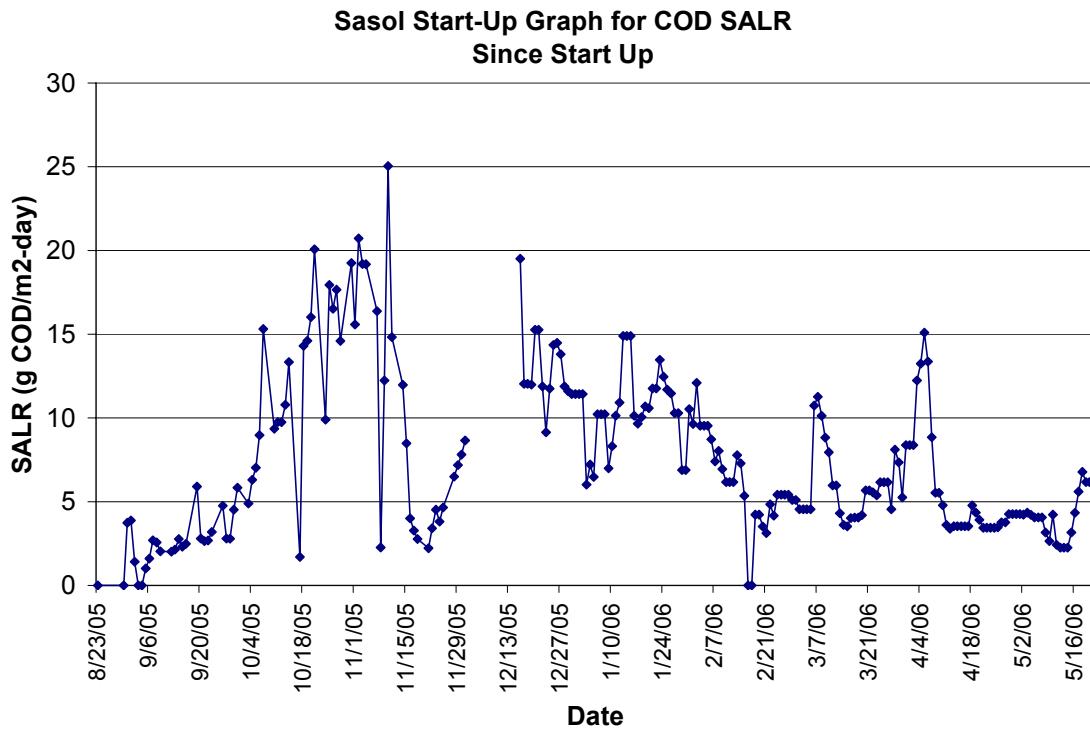


Figure 14 – Full Scale MBBR SALR vs. Time

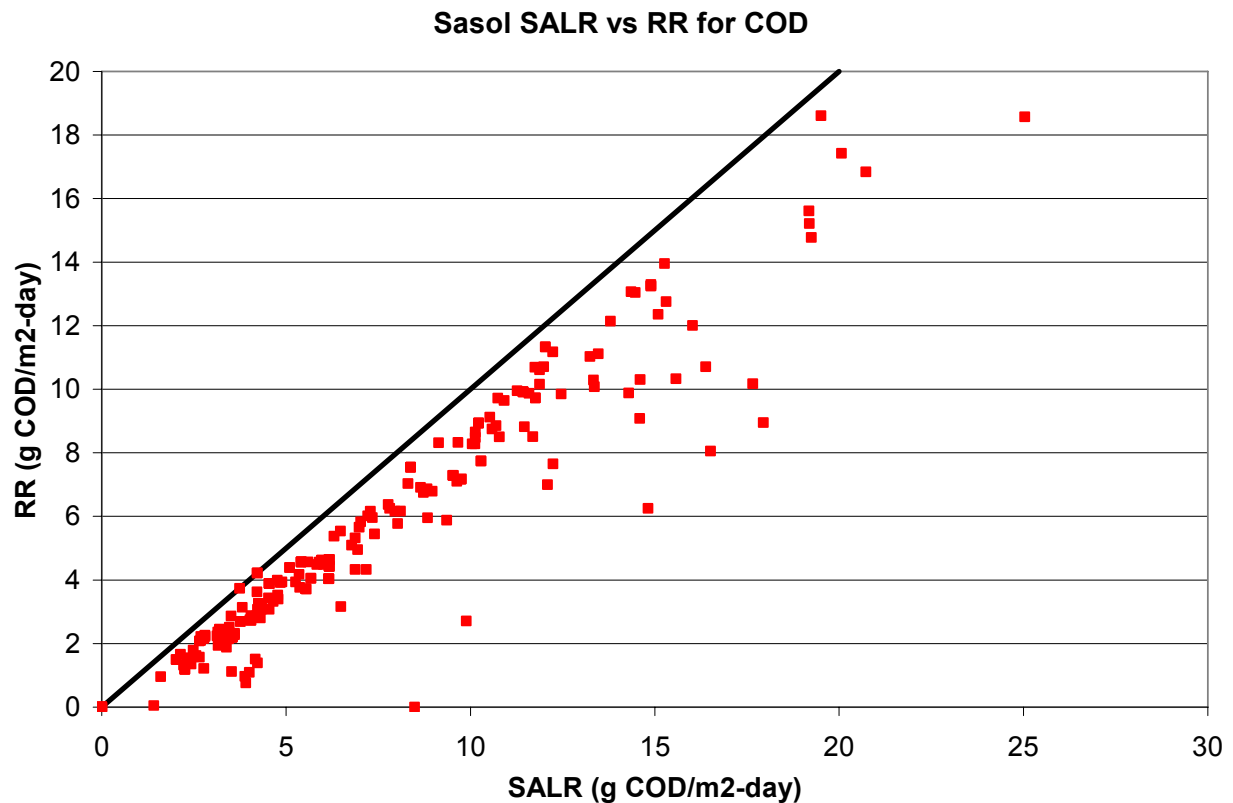
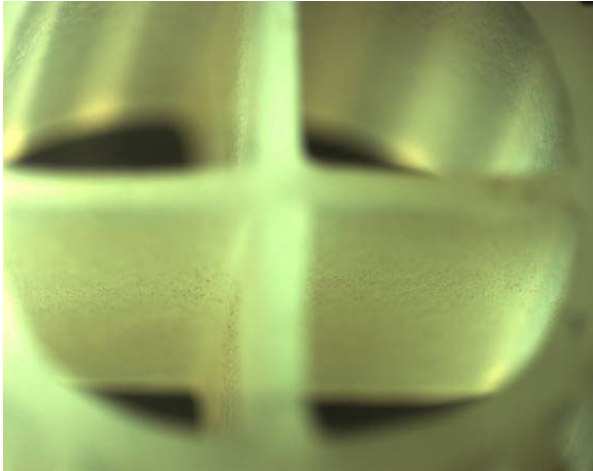


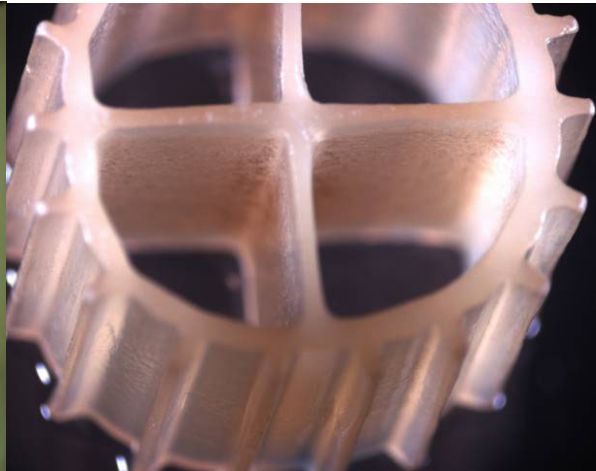
Figure 15 – Full Scale MBBR SALR vs. RR

Figure 15 takes the SALR from Figure 14 and adds the removal rate. Similar to the graph shown earlier from the pilot study, the MBBR is showing consistent removal of COD.

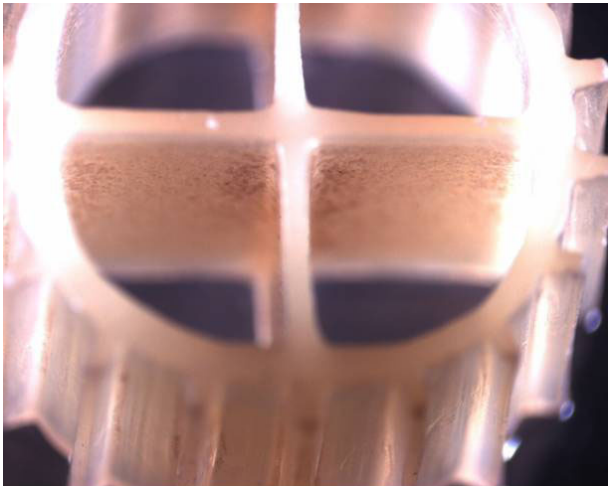
Start up of the MBBR pre-treatment system was also assessed by microscope evaluations. Figure 16 shows 4 different microscope photos showing how thin the biofilm was on the media, yet during each of these sample days, the MBBR efficiency was excellent. Overall SALR's during these time periods were 2 – 3 lb COD/1000 ft²-day (10 – 15 g COD/m²-day). Figure 17 shows the biofilm and scraping of the biofilm from 7 February 2006. The SALR during 7 February was < 2 lb COD/1000 ft²-day (10 g COD/m²-day).



a) 30 September, 2005



b) 9 December, 2005



c) 19 December, 2005



d) 16 January 2006

Figure 16 – MBBR K1 Media Micrographs of Biofilm

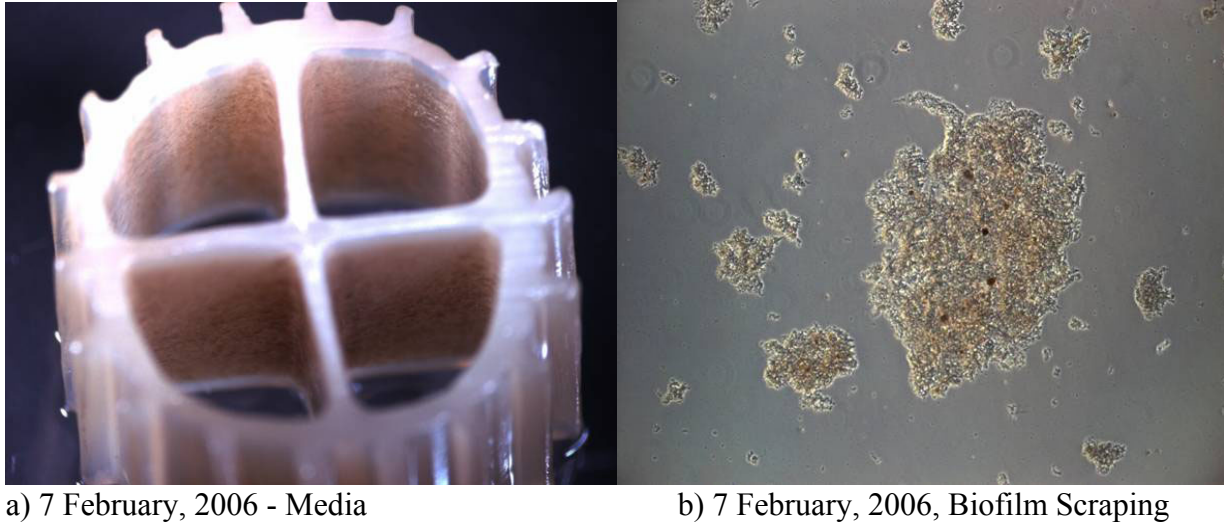


Figure 17 – MBBR K1 Media Micrographs of Biofilm with scraping on 7 February, 2006

Soon after the WRF achieved the performance test on the MBBR, the powdered activated carbon (PAC) was placed into the Aeration Tank to create a 2,000 ppm concentration in the vessel. This started the PAC treatment system into operation. The PAC system operated successfully achieving over 80% reduction of the COD coming from the MBBR and reducing the ammonia to less than 1 ppm during the steady operations in December and January.

During the commissioning of the WRF, Mr. Murphy, the creator of Murphy's Law (What can go wrong will go wrong), took up permanent residence at the WRF. His manifestations included:

- Collapse of the Chemical Treatment Clarifier after filling it with water on South African Freedom Day
- Loss of the Blowers motors with extended off site repairs twice during commissioning
- Stack damage to the Thermal Oxidizer due to a plug in the burner

Despite these obstacles, the WRF has maintained continuous operations through perseverance, rental compressors, and creative bypassing sections of the plant. The WRF is in the process of evicting Mr. Murphy from the facility and banning him from future entrance.

CONCLUSION

The new AnoxKaldnes MBBR + PAC treatment system installed at the Sasol WRF is successfully operating since its commissioning in August 2005. Results have shown the MBBR + PAC treatment system has met the overall treatment efficiency by reducing organic concentrations on average 95% and also provided for complete nitrification.

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