CHAPTER 4 : RESULTS AND DISCUSSION

4.0 WASTE STREAM CHARACTERISATION

The characteristics of the influent (raw waste water) and effluent emanating from the plant's existing waste water treatment facility are shown in **Table 4.1 and 4.2**. In principle, the concentration of the effluent emanating from the wastewater treatment plant should comply to the limits proposed by the Department of Environment (DOE), however certain parameters do not meet the proposed effluent standards. This study examines the possibility of treating the effluent emanating from the existing WWTP for recycling purposes instead of just upgrading the WWTP in order that the discharge parameters comply with local enforcement parameters. Major pollution parameters were analysed based on composite samples collected from the main effluent channel.

4.1 COAGULATION AND FLOCCULATION STUDIES

4.1.1 Optimising pH

Numerous jar tests were carried out in order to establish a practical understanding of the coagulation performance for this application. Initially the tests were carried out to determine the optimum pH for the function of alum. A fixed dose of alum was added to the effluent waste water and the pH of the mixture was then adjusted with calcium hydroxide and sulphuric acid. The efficiency of alum at various pH was measured in terms of turbidity. The studies showed that alum had the best removal efficiency at pH of 7.5. (**Figure 4.1**). Zeta potential measurement of effluent treated with alum at various pH confirmed that at pH between 4.0 – 5.0 the treated colloidal dispersion was

stable, however at pH between 7.0 – 7.5, destabilisation of the treated colloidal was observed as the Zeta potential approached zero. **(Figure 4.2)**

Table 4.1: Physico-chemical characteristics of the influent stream. (Raw waste water)

Parameters	**Unit**	**Minimum**	**Maximum**	**Average***	**Std. B****
PH		8.0	9.3	8.5	5.5-9.0
BOD_5 @ 20°C	mg/L	450	598	588	50
COD	mg/L	4500	5868	5632	100
TSS	mg/L	2784	3824	2864	100
Temperature	^0C	29.5	30.2	30.2	-
Turbidity	NTU	4896	5854	5632	-
DO	mg/L	0.05	0.79	0.58	-
Mercury as Hg	mg/L	0.012	0.035	0.031	0.05
Cadmium as Cd	mg/L	ND(<0.003)	ND(<0.003)	ND(<0.003)	0.02
Hexa-Chromium as Cr^{6+}	mg/L	ND(<0.02)	ND(<0.02)	ND(<0.02)	0.05
Cyanide as CN	mg/L	ND(<0.02)	ND(<0.02)	ND(<0.02)	0.10
Lead as Pb	mg/L	ND(<0.02)	0.15	0.12	0.5
Tri-Chromium as Cr^{3+}	mg/L	0.02	0.09	0.06	1.0
Copper as Cu	mg/L	ND(<0.003)	0.098	0.095	1.0
Manganese as Mn	mg/L	0.048	0.065	0.057	1.0
Nikel as Ni	mg/L	0.030	0.048	0.04	1.0
Tin as Sn	mg/L	ND(<0.01)	ND(<0.01)	ND(<0.01)	1.0
Zinc as Zn	mg/L	0.154	0.198	0.173	1.0
Boron as B	mg/L	1.3	1.9	1.7	4.0
Iron as Fe	mg/L	0.42	0.58	0.48	5.0
Phenol	mg/L	0.34	0.057	0.036	1.0
Free Chlorine as Cl_2	mg/L	ND(<0.02)	ND(<0.02)	ND(<0.02)	2.0
Sulphide as S^{2-}	mg/L	ND(<0.1)	ND(<0.1)	ND(<0.1)	0.5
Oil and Grease	mg/L	ND(<2)	ND(<2)	ND(<2)	10.0

* Average of 20 samples.

** DOE Std B parameter limits for discharge of effluent to inland waters below water intake points.

Table 4.2: Physico-chemical characteristics of the effluent stream

Parameters	Unit	Minimum	Maximum	Average*	Std. B**
PH		7.3	7.5	7.3	5.5-9.0
BOD_5 @ 20°C	mg/L	150	298	291	50
COD	mg/L	926	1468	1362	100
TSS	mg/L	1068	1128	1080	100
Temperature	^0C	29.5	30.2	30.2	-
Turbidity	NTU	1180	3740	2325	-
DO	mg/L	2.23	2.26	2.25	-
Mercury as Hg	mg/L	0.01	0.03	0.02	0.05
Cadmium as Cd	mg/L	ND(<0.003)	ND(<0.003)	ND(<0.003)	0.02
Hexa-Chromium as Cr^{6-}	mg/L	ND(<0.02)	ND(<0.02)	ND(<0.02)	0.05
Cyanide as CN	mg/L	ND(<0.02)	ND(<0.02)	ND(<0.02)	0.10
Lead as Pb	mg/L	ND(<0.02)	ND(<0.02)	ND(<0.02)	0.5
Tri-Chromium as Cr^{3+}	mg/L	0.015	0.25	0.02	1.0
Copper as Cu	mg/L	ND(<0.003)	ND(<0.003)	ND(<0.003)	1.0
Manganese as Mn	mg/L	0.025	0.035	0.032	1.0
Nikel as Ni	mg/L	0.01	0.03	0.01	1.0
Tin as Sn	mg/L	ND(<0.01)	ND(<0.01)	ND(<0.01)	1.0
Zinc as Zn	mg/L	0.033	0.085	0.067	1.0
Boron as B	mg/L	0.18	0.24	0.20	4.0
Iron as Fe	mg/L	0.20	0.98	0.32	5.0
Phenol	mg/L	0.006	0.016	0.008	1.0
Free Chlorine as Cl_2	mg/L	ND(<0.02)	ND(<0.02)	ND(<0.02)	2.0
Sulphide as S^{2-}	mg/L	ND(<0.1)	ND(<0.1)	ND(<0.1)	0.5
Oil and Grease	mg/L	ND(<2)	ND(<2)	ND(<2)	10.0

* Average of 20 samples.

** DOE Std B parameter limits for discharge of effluent to inland waters below water intake points.

4.1.2 Optimising Chemical Dosage

Experiments were carried out to determine the combined optimum dose of alum and polyelectrolyte. Initially the optimum dose of alum was determined. The coagulation and flocculation of wastewater was investigated using alum doses of 100-1000 mg/L. The pH was kept constant at 7.5 by using either calcium hydroxide or sulphuric acid. Coagulated wastewater samples were tested for residual suspended solids after a 1 hour settling period (measured as turbidity) and COD. The results of alum coagulation treatment for wastewater are shown in **Figure 4.3** and **Figure 4.4**. The studies showed that a relatively low aluminium ion dosage of 700 mg/L was capable of reducing turbidity and COD load from the wastewater by coagulation to an acceptable level. Relative turbidity, T/T_0, where T_0 is T in the absence of coagulant, was employed in order to assess the efficiency of the coagulant used. At the optimum dosage of about 700 mg/L the COD removal rates were 65% while the relative turbidity was 12.8%. Addition of polymer concentration between 1-10 mg/L at optimum alum dosage of 700 mg/L further enhanced COD and turbidity removal rates. Maximum COD removal rates of 74% was observed at polymer concentration of 6 mg/L at optimum alum dosage of 700 mg/L. Relative turbidity (T/T_0) decreased from 12.8% to 0.37%. **(Figure 4.5 and Figure 4.6)**

4.1.2.1 Effect of Alum Dosage

As the concentration of aluminium salt used as the primary coagulant was increased from 100mg/L to 700mg/L, it was observed that there was a corresponding increase in the COD and suspended solids (measured as turbidity) removal rates. However, as the coagulant concentration was increased above 700mg/L, no increase in COD and

suspended solids removal rates were observed. This phenomenon can be explained by examining the coagulation mechanism of the aluminium salt.

Paint waste water contains colloidal suspended solids that are difficult to remove. Owing to their small size, large specific surface area and relatively high electric charges, these particles interact with the water molecules. This special interaction imparts amongst others a high aggregative stability to the colloidal particle. However, the stability of the colloidal dispersion diminished upon addition of the aluminium salt.

Over the years many coagulation mechanisms have been proposed. Towards the end of the last century, Al^{3+} ions were believed responsible for destabilising and coagulating colloidal particles. Mattson (1928) attributed coagulation of the suspended solids mainly to the hydrolysis products of the Al^{3+} ions, aluminium hydroxide. In the sixties, it was believed that the principal agent destabilising the colloidal dispersion and removing the bulk of the dissolved organics were the polynuclear (containing several Al atoms) and the electrically unsaturated (positively charged) aluminium(III) hydroxides. This theory implies that no compounds of the formula $Al(OH)_3$ develop during the clarification process. Parthasarathy and Buffle (1985) demonstrated experimentally the presence of a water soluble complex $[Al_{13}(OH)_{32}]^{7+}$ which is believed to be a very highly effective coagulant. Packham (1962) suggested the rate at which aluminium hydroxide precipitates determines the extent to which the colloidal dispersion is coagulated. It was noted that at pH 7.0 aluminium hydroxide precipitated the fastest. This implies that the mechanism destabilising the dispersion consists of the suspended solids being entrained by the precipitating aluminium hydroxide, referred to

as sweep coagulation. According to Gregory (1978), under particular conditions both the aluminium ions, the $[Al_4(OH)_8]^{4+}$ complexes (specific adsorption) and the $Al(OH)_3$ compounds (sweep coagulation) play a role in coagulating the dispersion, depending on the aluminium salt added, the pH and the concentration of the suspended solids. Avner and Takashi (1998) concluded that coagulation can be effected by double layer compression, adsorption, charge neutralisation and sweep coagulation and inter particle bridging.

Based on earlier available information, Licsko (1997) proposed that the destabilisation and coagulation process could be explained by one of the four possible distinct mechanisms of coagulation described below.

a. The Al^{3+} ions added to the water are adsorbed on the surface of the colloidal particles which carry a high negative electrical charge, and this alters the electric charge of the solids and lowering their Zeta-potential to zero. The electrostatic repulsion forces between the particles are thus minimised allowing the particles to aggregate.

b. Owing to partial hydrolysis of the Al^{3+} ions water-soluble aluminium - hydroxide complexes are formed, which contain a few Al atoms and which carry a positive charge. These complexes enter into durable bonds with the negatively charged particles (they are adsorbed on the surface of the latter) changing thus their originally high surface charge (reducing it virtually to zero). The particles aggregate thereafter.

c. Hydrolysis of the Al^{3+} ions produces within a brief period of time (a few seconds) aluminium hydroxide sols which contain much water and carry a positive charge. These sols contain particles which during the seconds following their development are smaller than the colloidal particles to be removed. The sols are therefore adsorbed on the solid particles present in surface waters, changing the high negative electric charge of the latter. The ensuing metal hydroxide - solid particle complex has a resultant electric charge of the -5.0 - 0.0 mV Zeta potential order and is thus suited to effective, rapid aggregation.

d. The hydrolysis products of the Al^{3+} ions aggregate at high rates into large aluminium hydroxide flocs, which owing to their large size "enmesh" or "sweep" the colloidal particles to be removed (sweep coagulation).

The laboratory experiments demonstrated that between pH 5.0-6.0, the removal of suspended solids was not effective. However between pH 6.5 – 7.5, efficient removal of the suspended solids was observed.

Experiments conducted by Licsko (1997) demonstrated similar results. In the low pH range ($4.0<pH<5.0$), the amount of aluminium salt needed to change the electric charge of the particles in the colloidal dispersion was considerably larger than that in the neutral pH range ($7.0<pH<7.5$), where the development of the aluminium hydroxides predominates (Prieşing, 1962). This is because in the low pH range ($4.0<pH<5.0$) the stability of the aluminium ions is high and are therefore not

transformed into aluminium hydroxide. From this, Licsko (1997) concluded that at relatively elevated pH and buffering capacities, it is unlikely for process "a" and "b" to be the principal destabilising mechanism as experiments have shown that 97% of the aluminium ions introduced, convert to poorly water soluble aluminium hydroxide.

Qualitative experiments performed by Licsko (1997) employing a model system containing Ca^{2+}, Mg^{2+}, HCO_3^-, Na^+ and Cl^- ions (but no suspended solids) in distilled water to which aluminium salt was added, showed that within a few seconds large aluminium hydroxide flocs developed. The flocs were removed from the water, taking care not to break them up and then introduced into a surface water sample containing suspended solids. The large aluminium hydroxide flocs had no influence on the electric charge of the suspended particles and failed also to reduce the turbidity of the water.

The experimental data described above demonstrate the inability of the large flocs to participate in the destabilisation of the colloidal dispersion. The large flocs are unsuited to establishing durable bonds with the suspended solids. From the model system, Licsko (1997) concluded that mechanism "d" of destabilising the colloidal dispersion is unacceptable, instead he concluded that the large flocs contribute at the most to the aggregation process of the smaller aluminium hydroxides.

From his experiments, Licsko (1997) concluded that the destabilisation and coagulation mechanism was due to hydrolysis followed by the development of mostly dissolved, positively charged aluminium hydroxide complexes. The dissolved metal hydroxide complexes then enter into bonds and become adsorbed onto the solid

particles of the colloidal dispersion, changing their high negative charge, a prerequisite for subsequent aggregation. The dissolved metal hydroxides may also polymerise, which is the aggregation of water soluble complexes to produce positively charged, poorly water soluble aluminium (III) hydroxide sols. These sols are also capable of entering into bonds and become adsorbed onto the solid particles of the colloidal dispersion, changing their electric charge and thus promote aggregation. These processes are favourable in water treatment. The sols are also capable of aggregating regardless of their identical electrical charges mainly by hydrogen bonding. This kind of aggregation is however unfavourable in that no solid particles of the colloidal dispersion are involved, leading thus to a waste of coagulant.

An increase in the concentration of alum salt at optimum pH 7.5 did not enhance suspended solids and COD removal rates. This could possibly be due to the unfavourable aggregation of the aluminium hydroxide sols without involving solid particles of the colloidal dispersion. For efficient removal of suspended solids, bonds must be established between the positively charged water soluble aluminium hydroxide complexes, the positively charged aluminium hydroxide sols (poor solubility) and the solid particles of the dispersion. The hydrolysis of the aluminium ions should be accelerated while the sol aggregation and floc growth stage should be retarded following the introduction of the coagulant. This can be accomplished by rapid mixing of the coagulant.

4.1.2.2 Effect of Polymers

The addition of polymer in combination with alum at 700 mg/L at pH 7.5 enhanced treatability of the effluent. The removal of COD load and turbidity increased with the amount of polymer added. However, treatability became limited as polymer concentration reached a critical value: 6 mg/L of polyacrylamide was sufficient to enhance the removal efficiency of COD from 65% to about 74%. Relative turbidity measured in terms of T/T_0 decreased from 12.8% to 0.37%. **(Figure 4.5 and Figure 4.6)**.

According to theoretical considerations and the foregoing experimental results alike, the stability of the colloidal dispersion is reduced mainly by the positively charged, poorly water soluble aluminium hydroxide sols which are short lived. The sols are capable of aggregating to form microflocs or pinflocs. The high molecular weight polymers are capable of bridging and mechanically and chemically binding microflocs together.

Upon addition of polymer, development of the flocs are followed immediately by two simultaneous processes. Agglomeration in which microflocs are attached together forming larger particles called flocs and physical entrapment as the large flocs settle. As flocs begin to settle, they capture smaller microflocs further improving suspended solids and COD removal.

The combined dose of alum and polymer achieved better removal of colloidal particles from wastewater compared to either chemical coagulants or polyelectrolyte used alone

(**Figures 4.4 and 4.6**). Studies by Turkman (1991) showed that the application of polymeric coagulants could contribute to increased removal efficiency.

4.2 CROSS-FLOW MICROFILTRATION

Cross-flow microfiltration was employed as the polishing treatment for the effluent to recover process water for reuse in the manufacturing process. Initial studies were carried out to determine whether cross-flow microfiltration treatment of the effluent without chemical pretreatment could be employed. In subsequent studies, the effluent that had undergone coagulation-flocculation pretreatment was passed through the cross-flow microfiltration unit. The cross-flow microfiltration unit consisted of a cellulose acetate membrane with pore size 0.2 μm, an effective area of $0.08m^2$ and a transmembrane pressure of 0.3 bar.

Cross-flow microfiltration of the chemically treated effluent from the WWTP produced good quality permeate that could be recycled for various uses within the manufacturing plant. The filtered water, which is free of suspended matter, bacteria and colloidal matter, is ideal for reuse and this reduces water consumption and liquid discharge to external watercourses.

Cross-flow microfiltration has been used to remove a variety of pollutants in water and waste water treatment since it can remove particles in the range of 0.1 – 10 μm. However, the accumulation of rejected material on the surface of the membrane frequently leads to a decline in the permeate flux over time. Significant work has been pursued to avoid or reduce its severity. They can be grouped into three major

approaches: hydrodynamic (changing flow regime across the membrane surface), surface modification (changing the surface/foulants affinity) and regular cleaning (Howell, 1992).

Aimar and Howell (1989) proposed that the flow of material can better be controlled by a constant flux during the filter run since the convective flow of solute towards the membrane is then constant throughout the run. The critical flux hypothesised by Field at al. (1995) states that there exists a flux below which a decline of flux with time does not occur but above this flux, fouling of the membrane is observed. The hypothesis of critical flux or limiting flux suggests that a flux exists which is equivalent to the corresponding clean water flux at the same transmembrane pressure. Studies conducted by Kwon at al. (1996) indicated that critical flux was significantly affected by the size and concentration of particles in suspension and by crossflow velocity.

4.2.1 Membrane filtration without pre-treatment

Several experiments were conducted without pre-treatment of effluent water to check the ability of membrane filtration to remove COD, turbidity and microorganisms in the effluent and to investigate the effect on the limiting flux in cross-flow microfiltration. **Table 4.3** shows the solids removal efficiency in terms of turbidity at different feed flowrates while **Table 4.4** shows the COD removal efficiency at different flowrates. **Figure 4.7** presents the limiting flux as a function of time. The solids removal was practically complete as shown in **Table 4.3**. (Removal of bacteria from the effluent water will be discussed in Section 4.4.)

Table 4.3: Turbidity of influent and permeate (without pre-treatment)

Influent (NTU)	Feed Flowrate (L/hr)	Permeate (NTU)	Removal Efficiency
1080	45	9.97	99.07
	54	10.97	99.98
	75	10.80	99.00

Table 4.3 shows that the initial turbidity was removed effectively from the untreated effluent water but a decrease in the permeate flux was observed after 20 minutes as shown in **Figure 4.7**.

Table 4.4: COD concentration of influent and permeate (without pre-treatment)

Influent COD (mg/L)	Feed Flowrate (L/hr)	Permeate COD (mg/L)	Removal Efficiency
1362	45	209	84.65
	54	200	85.32
	75	205	84.95

4.2.2 Membrane filtration with pre-treatment

4.2.2.1 Effect of flocculation

A set of experiments was conducted with effluent water at different feed flowrates to study the effect of chemical pre-treatment on the limiting flux of the membrane filtration process. A more gradual decrease in the flux rate was observed **(Figure 4.8)** as compared to the flux decline observed with the untreated waste water sample. The

decline in flux after a 1 hour period was however nearly the same for both cases. In both cases the initial flux was nearly halved. The absolute flux values (at start of operation) were however about twice higher with the pre-treated feed as shown in **Table 4.5**.

Table 4.5: Effect of Flocculation/pre-filtration on limiting flux

Feed Flowrate (L/hr)	Absolute Limiting flux ($L/m^2/h$)	
	Without Treatment	With Treatment
200	17.45	36.45
300	22.68	43.93
400	27.85	59.18

A comparison between **Figure 4.7** and **Figure 4.8** clearly shows that the initial flux was significantly higher with the pre-treated effluent and although the decline in flux was almost the same in both cases, the flux values for the pre-treated effluent was significantly higher than that of the untreated effluent. This would suggest that the osmotic backpressure was higher with the untreated effluent. Also, the flux reduction after 60 minutes, was almost similar in both cases. This suggests that concentration polarisation is the main difference between the two cases.

All membrane separations rely on a driving force across the membrane to induce the flow or flux and a separation factor, which prevents some materials from crossing. The driving force for flow differs for different systems. Some systems are pressure driven while others are concentration driven, some systems may also be partially pressure and

partially concentration driven. Membrane filtration is a totally pressure driven system. Pressure is employed as the driving force that effects separation of the solid – liquid phase. The driving force overcomes osmotic pressure effects, drag of solvent through the membrane and resistance of fouling layers and deposits on the membrane surfaces. In pressure driven separations, there is an effective limit to the fluxes which can be achieved (Bilstad, 1997). There are two major external influences which alter the selectivity and adversely affect the flux of membrane; concentration polarisation which is short term and recoverable and membrane fouling which is long term and frequently permanent (Bell and Cousins, 1994).

Concentration polarisation is caused by rejection of retained solute. This causes a concentration build up in the region of the membrane surface. which in turn causes an osmotic pressure resistance build up at the membrane surface. This affects the flux properties of the membrane (Bilstad, 1997). The untreated effluent contain higher levels of suspended solids. As such the concentration build up in the region of the membrane surface is higher and therefore the osmotic backpressure is higher resulting in lower fluxes.

Membrane fouling on the other hand causes a gradual decline of flux with time. Flux decline is caused amongst others, by slime accumulation due to bacterial growth, deposition of organic macromolecules, colloidal deposition and physical compaction of the membrane material.

4.3 SCALE UP OF JAR TESTING STUDIES

4.3.1 Scale up of Chemical Treatment Studies

Using optimum dosage of alum and polyelectrolyte obtained from the jar test experiments, a scale up of the experiment using 10 litres of waste water was undertaken. The trial confirmed the values obtained in the jar test for optimum removal of COD and turbidity. Characteristics of the effluent after coagulation-flocculation treatment employing a combined dose of alum, calcium hydroxide or sulphuric acid and polymer are shown in **Table 4.6**.

4.3.2 Cross-flow Microfiltration Studies of 10 Litre Batch

The chemically treated effluent was then passed through a cross-flow microfiltration unit. The characteristics of the effluent after coagulation – flocculation and membrane treatment are shown in **Table 4.7**.

Table 4.6: Physico-chemical characteristics of effluent after coagulation-flocculation treatment

Parameters	**Unit**	**Sample**	**Std. B****
PH		7.5	5.5-9.0
BOD_5 @ 20°C	mg/L	96.7	50
COD	mg/L	354.12	100
TSS	mg/L	8	100
Temperature	^0C	27.0	-
Turbidity	NTU	8.6	-
DO	mg/L	7.03	-
Colour	True Colour Units	5	-
Mercury as Hg	mg/L	0.012	0.05
Hexa-Chromium as Cr^{6+}	mg/L	ND(<0.02)	0.05
Cyanide as CN	mg/L	ND(<0.02)	0.10
Lead as Pb	mg/L	ND(<0.02)	0.5
Copper as Cu	mg/L	0.019	1.0
Zinc as Zn	mg/L	0.121	1.0
Iron as Fe	mg/L	0.10	5.0

** DOE Std B parameter limits for discharge of effluent to inland waters below water intake points.

Table 4.7: Physico-chemical characteristics of effluent after coagulation-flocculation and membrane treatment.

Parameters	Unit	Sample	Std. B**
PH		7.5	5.5-9.0
BOD_5 @ 20°C	mg/L	28	50
COD	mg/L	65	100
TSS	mg/L	5	100
Temperature	^0C	27.0	-
Turbidity	NTU	0.3	-
DO	mg/L	7.25	-
Colour	True Colour Units	5	-
Mercury as Hg	mg/L	0.01	0.05
Hexa-Chromium as Cr^{6+}	mg/L	ND(<0.02)	0.05
Cyanide as CN	mg/L	ND(<0.02)	0.10
Lead as Pb	mg/L	ND(<0.02)	0.5
Copper as Cu	mg/L	0.006	1.0
Zinc as Zn	mg/L	0.10	1.0
Iron as Fe	mg/L	0.03	5.0

** DOE Std B parameter limits for discharge of effluent to inland waters below water intake points.

4.4 MICROBIOLOGICAL STUDIES

The effluent samples were tested for microbiological contamination. Two sets of samples were collected and subjected to chemical pre-treatment and microfiltration as described earlier. Effluent samples before and after chemical pre-treatment as well as after microfiltration were collected and tested for microbiological contamination.

Six samples labelled A_1, A_2, A_3, B_1, B_2 and B_3 were examined for microbiological contamination. Sterile distilled water was used as a control in the tests. Description of the samples are given below:

A_1 & B_1	=	Effluent samples
A_2 & B_2	=	Effluent samples after chemical pre-treatment
A_3 & B_3	=	Effluent sample after chemical pre-treatment and microfiltration

Initially the pH and redox potential of each sample were determined at ambient temperature. The samples were then screened for aerobic microbes and anaerobic sulphate reducing bacteria. Samples showing positive results during the screening process were then subjected to a total viable count employing the Miles and Misra technique.

4.4.1 Determination of pH Measurement and Redox Potential

The pH measurement and redox potential of the samples are shown in **Table 4.8** below.

Table 4.8: pH and redox potential measurements of samples and control.

Sample	pH	Redox Potential
A_1	7.14	-45
A_2	7.18	-45
A_3	7.18	-48
B_1	7.30	-41
B_2	7.38	-45
B_3	7.47	-53
Distilled Water	6.12	+19

The pH of the samples were generally neutral, ranging from 7.14 to 7.47. The negative redox potential recorded, indicate that the samples contained mild reducing substances. This information is necessary if biocides were to be added to disinfect the water samples.

4.4.2 Screening for Microbial Contamination

The six water samples and distilled water used as a control, were screened for aerobic and anaerobic microbial contamination. Screening for aerobic microbes were conducted by streaking the samples onto nutrient agar incubated at 25°C and 30°C to detect bacterial growth and onto malt extract agar incubated at 25°C to detect fungi growth. After incubation for at least 48 hours the resultant microbiological growth was visually assessed using the rating scale as detailed in **Table 4.9**. SIM/Iron Sulphite Agar (ISA) tubes were used for screening of anaerobic microbes or more specifically sulphate reducing bacteria (SRB). The tubes were incubated at 30°C and any resultant growth were assessed visually according to the degree of black coloration developing. The results of the screening test are as shown in **Table 4.9**

Table 4.9: Screening for aerobic and anaerobic microbes

Samples	Microbiological Growth Rating On* :			
	Nutrient Agar[1]		Malt Extract Agar[2]	ISA Tubes[3]
	25°C	30°C	25°C	30°C
A_1	6	6	0	0
A_2	3	4	3[b]	0
A_3	0	0	0	0
B_1	6	6	6[b]	0
B_2	6	6	6[b]	0
B_3	0	0	0	0
Distilled Water (Control)	0	0	0	0

NB. *Growth Rating Scale: 0 = No growth 6 = dense growth

[1] Nutrient Agar for detection of bacteria

[2] Malt Extract Agar for detection of fungi (including yeast)

[b] = bacteria

*Growth Rating Scale: 0 = No growth +++ = Dense growth

[3] ISA (Iron Sulphate Agar) tubes for detection of sulphate reducing bacteria.

Microbiological growth were observed for samples A_1, A_2, **(Photograhps 1 – 4)** and samples B1, B2. **(Photographs 5 - 7)**. Samples A3 and B3 **(Photoghaphs 8 – 11)** as well as the control showed no microbiological growth. Positive microbial growth on malt extract agar plates were identified as bacterial and not fungi growth. All ISA tubes showed negative results indicating no growth of sulphate reducing bacteria.

4.4.3 Total Viable Count by Miles and Misra Technique.

Samples showing positive results in the screening stage were subjected to a total viable count to assess the extent of microbiological contamination of the samples. Results of the total viable count are shown in **Table 4.10**.

The concept of enumeration of viable microorganisms is based on the assumption that each microorganisms will give rise to one visible colony after incubation on a solid medium. The number of colonies from a countable drop were calculated based on the following equation.

Organisms/ml = mean CFU's (Colony Forming Units) x dilution

Example :

For instance, if in the 1 in 100,000 (10^{-5}) dilution sector, 22 and 26 colonies were counted respectively from the 25 µl (0.025ml) aliquots of inoculum, thus :

$$\frac{22+26}{2} \times \frac{10^5}{0.025} = 9.06 \times 10^7 \text{ CFUs per ml}$$

Therefore it can be assumed that in 1 ml of sample contained 9.06×10^7 viable microorganisms.

Table 4.10: Screening of Total Viable Counts by the Miles and Misra Technique

Samples	Microbiological Growth Rating On* :		
	Nutrient Agar[1]		Malt Extract Agar[2]
	25°C	30°C	25°C
A_1	$>10^8$	$>10^8$	0
A_2	$2.4x10^4$	$2.8x10^5$	$1.8x10^{4b}$
A_3	0	0	0
B_1	$3.4x10^7$	$1.2x10^8$	$2.8x10^{6b}$
B_2	$7.2x10^7$	$6.6x10^6$	$5.6x10^{6b}$
B_3	0	0	0
Distilled Water (Control)	NT	NT	NT

N.B. NT = Not Tested

[b] = bacteria

As expected samples A_1 and B_1, (**Photographs 12 – 13** and **14 – 15**) collected form the WWTP were heavily contaminated with microbiological growth. Viable organisms present ranged from 10^7 to above 10^8 microorganisms per ml of sample.

Samples A_2 and B_2, (Photographs **16 – 17** and **18 – 19**) consisting effluent samples which have been chemically treated similarly show heavy growth of microorganisms. Viable microorganism counts range from 2.40×10^4 to 7.20×10^7.

Samples A_3 and B_3, (**Photographs 20 – 21** and **22 – 23**) consisting effluent samples which have undergone chemical treatment and membrane filtration, did not show any bacterial contamination.

It can be concluded from the tests above that chemical treatment alone is not capable of removing bacteria from the effluent. However, cross-flow membrane filtration is capable of removing bacteria to produce water that is of sufficient quality for use within the plant. The cross-flow microfiltration unit employing a cellulose acetate membrane with a pore size of 0.2 μm is capable of removing the smallest bacteria, *Pseudomonas diminuta* which has a diameter of 0.2 μm.

Reuse of the tubing system and the cellulose acetate membrane can however cause contamination of the permeate. This can be overcome by passing alcohol or steam through the system prior to use.

4.5 WATER BALANCE

4.5.1 Water Reuse Strategies in the Plant

10.96% of the raw water input is consumed for paint production while 89.04% ends up in the waste water treatment plant (WWTP). The amount of wastewater that goes to the WWTP daily is 56.875m^3/d. If this amount of water undergoes further treatment, then this can be recycled back to the plant and the total amount of raw water consumption can be reduced significantly. Apart from this, employment of a technology that will polish the wastewater treatment plant effluent before it gets discharged to the receiving waters will help conserve precious water reserves.

Microfiltration of WWTP effluent can give good quality permeate that can be recycled for various uses within the plant. Microfiltered water which is free of suspended materials, bacteria and colloidal matter is ideal for reuse outside the main production

line which do not require high quality water. It can also be used in the canteen for washing of floors and drains and in the laboratories for washing of mixing vessels, brushes and other equipment.

The reuse of microfiltered effluent can effectively reduce the raw water consumption. About 51.8% of the current WWTP effluent can be directly reused for some of the plants need.

4.5.2 Water Balance

The overall water usage within the production plant is shown in **Figure 4.9**. On an average of 63.875 m^3/d, only about 7m^3 is directly used for the production of paints, there is no waste water emanating from this activity. The quality control laboratory consumes about 25m^3 of raw water while the rest is utilised by the canteen, R & D laboratory, the packing area and in the washing of mixing apparatus, tanks and sieves.

As can be seen for the water balance (**Figure 4.10**) the canteen, R & D laboratory, the packing area and the washing of mixing apparatus, tanks and sieves, has the highest demand for water. Among the three areas, the washing of mixing apparatus, tanks and sieves is the largest water consumer. This activity also generates the largest amount of waste water compared to other activities in the plant. Therefore, it is seen that a great potential for water conservation lies in purifying and recycling the waste water mainly from paint wash up and a minor portion from other activities instead of releasing it to the public sewers.

It was observed from the present work that waste water from the manufacturing of paint can be treated by membrane filtration after chemical treatment for reuse. The study also showed that it was economically feasible as there were considerable savings from reduction in consumption of potable water. Conceptually the cross-flow microfiltation process will produce a permeate quality that is acceptable for reuse in the plant for various activities.

The application of chemical treatment and cross-flow microfiltration is able to recover 54.45% of waste water from the WWTP which would otherwise be discharged directly to public sewers. Assuming an overall yield of 60% for the CFMF system, then a total of 30.97 m^3/d of water can be recycled back into the plant for various uses daily. This reduces the input of potable water by 33.%.

The monthly consumption of raw water averages about 1278m^3. The recycling process is able to recover about 620 m^3/month. This would reduce the raw water intake by almost half and at the same time bring about some cost savings for the company. Most importantly however, is the reduction of waste water being discharged to public sewers. The installation of a cross-flow microfiltration unit and upgrading of the existing treatment plant would incur substantial cost initially. In the long term however, low maintenance cost of the filtration unit and low chemical cost for the chemical treatment of the process can bring about cost savings for the company.

4.6 RESIDUAL DISPOSAL FROM CROSSFLOW MICROFILTRATION

Concentration polarisation and membrane fouling are problems inherent to high performances in membrane systems. The use of cross-flow filtration as opposed to dead-end filtration to overcome these problems have been reported by many researches. (Chaize and Huyard, 1991; Kimura, 1991; Aya, 1994; Muller et.al., 1995). Maintaining high cross-flow velocities however, require high energy inputs which makes the process not feasible economically. To ensure high performance of the system, frequent cleaning with chemicals or backflushing with permeate is required.

Residual disposal for microfiltration (MF) and ultrafiltration (UF) systems are less critical compared to nanofiltration (NF) and reverse osmosis (RO) systems (Adham et al., 1996). Residuals from the MF system consist of chemical cleaning solutions, backwash water applied periodically to remove accumulated solids from the membrane surface and if applicable the crossflow recirculation. The backwash water of low pressure membrane systems is similar to the feedwater in terms of dissolved mineral quality, but the backwash water contains greater concentrations of microorganisms and particles (Adham et al.; 1996).

In most cases, backwash water is recycled to the influent plant after settling. The same can be applied for the present system. The settled solids can then be dewatered by a filter press which is currently being used to dewater sludge from the existing chemical treatment plant. The dewatered sludge can then be packed into drums and disposed off at a waste disposal facility.

Detergents are usually use for cleaning of membrane. The wash water generated from the cleaning process is neutralised before being discharged to the influent plant after a period of settling. Similarly, the sludge produced is dewatered and disposed off at a waste disposal facility.

4.7 CLEANING AND MAINTENANCE OF MEMBRANE

The CFMF feedwater is derived from effluent that has undergone chemical coagulation. The bulk of the dissolved solutes would have been removed during chemical coagulation. This would greatly reduce fouling and extend the life span of the membrane.

However to ensure a steady-state permeat flux level, regular backflushing of the membrane with the permeate and cleaning with chemicals is required. The membranes can be washed using 5% HCL solution or by using dilute NaOH solution at 40°C.

In this experiment, the membrane sheets were soaked overnight in 5% HCL solution and then washed with water. The procedure was able to restore permeate flux to original levels.

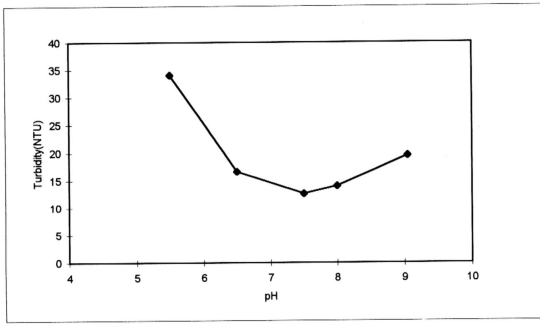


Figure 4.1: Turbidity readings vs. pH of waste water

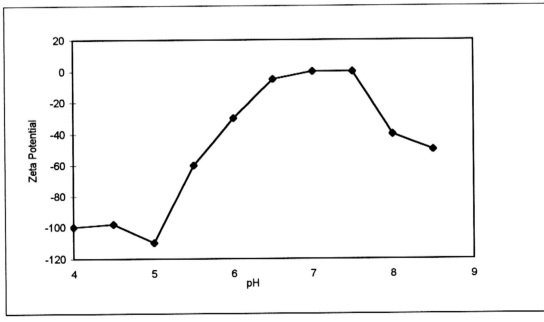


Figure 4.2: Zeta potential vs pH of effluent treated with alum

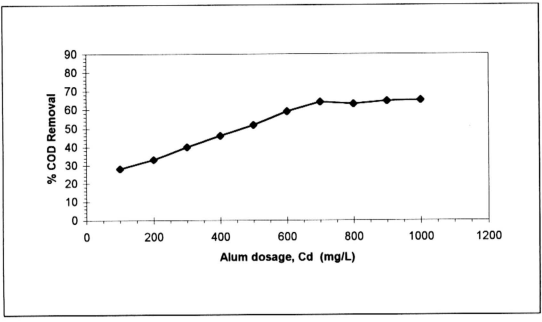


Figure 4.3: Percent COD removal versus alum dosage

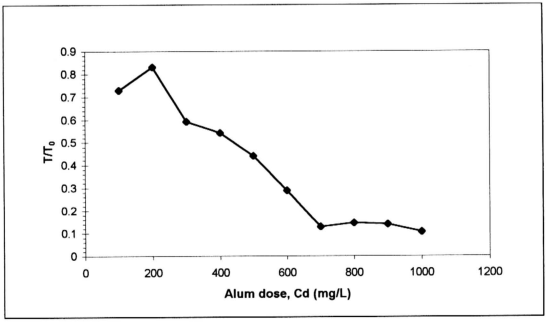


Figure 4.4: Relative turbidity vs alum dosage

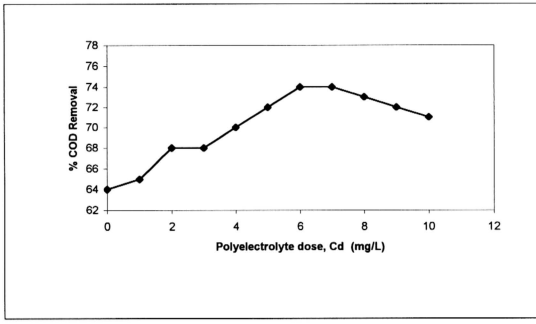


Figure 4.5: Percent COD removal versus polyelectrolyte dosage at optimum alum dose of 700 mg/L

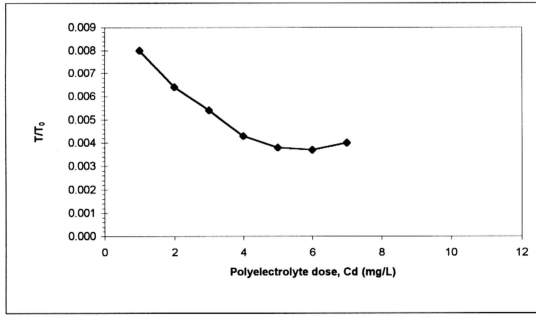


Figure 4.6: Relative turbidity versus polyelectrolyte concentration at optimum alum dose of 700 mgL

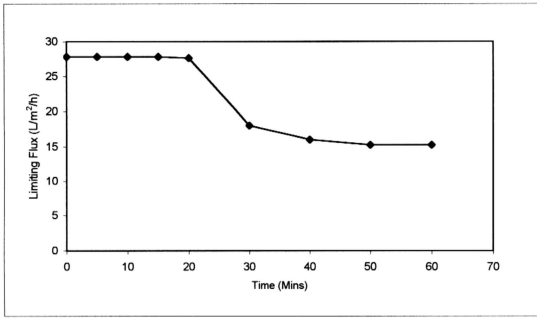


Figure 4.7: Effect of untreated effluent on limiting flux vs. time @ 400 L/hr feed flowrate.

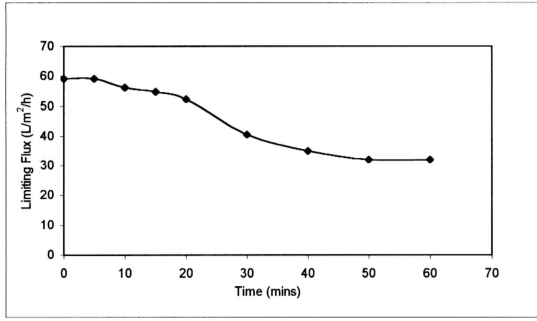


Figure 4.8: Effect of chemically treated water on limiting flux vs. time @ 400 L/hr feed flo

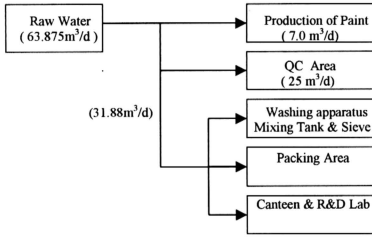


Figure 4.9: Overall water usage balance in the plant

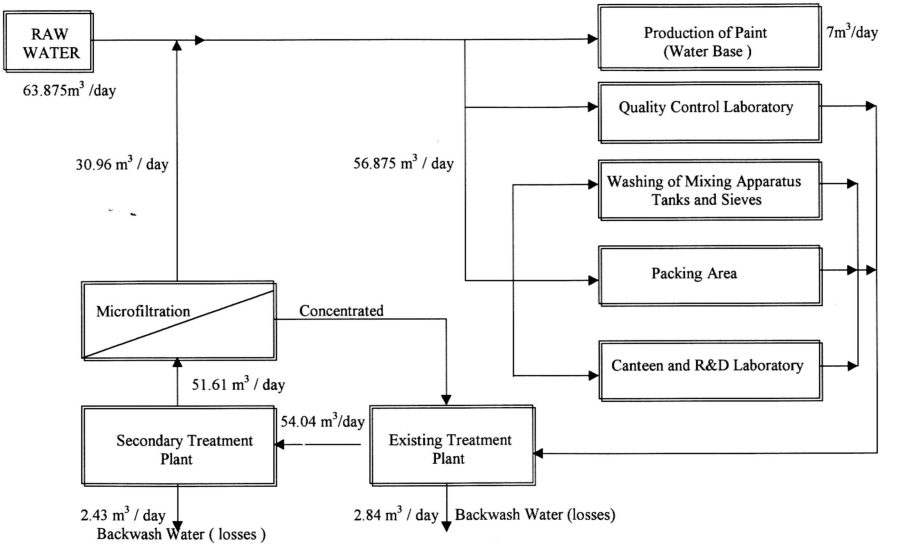
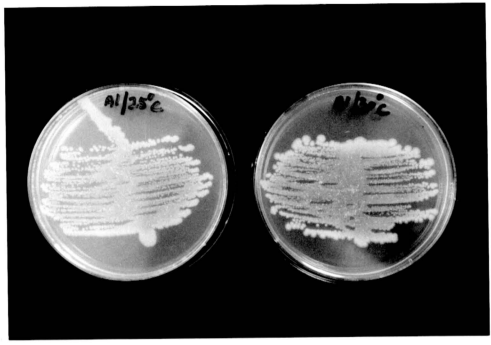
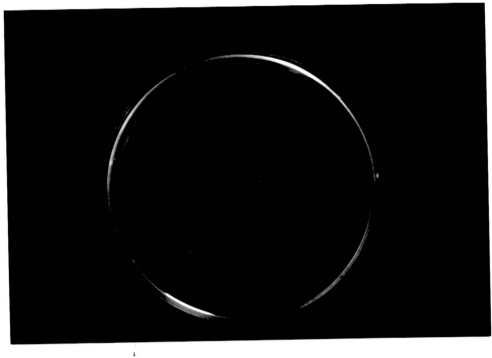


Figure 4.10 : Water balance

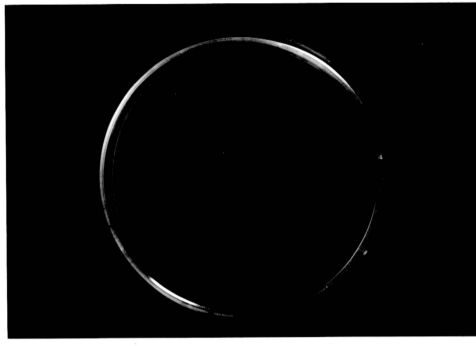


Photograph 1 : Microbiological growth observed on nutrient agar plates streaked with sample A_1 (effluent sample)

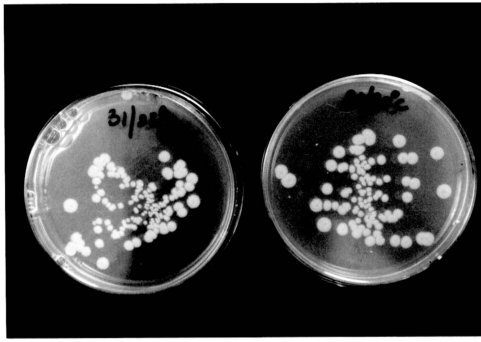


Photograph 2 : Microbiological growth observed on malt extract agar plates streaked with sample A_1 (effluent sample)

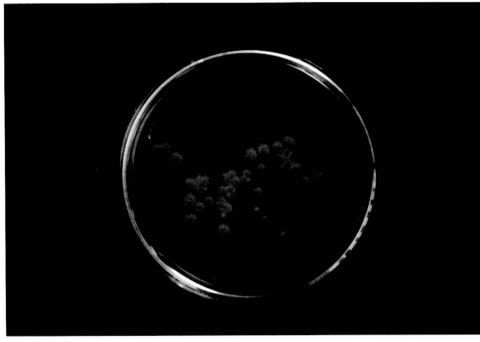
Photograph 3 : Microbiological growth observed on nutrient agar plates streaked with sample A_2 (effluent sample after chemical coagulation)



Photograph 4 : Microbiological growth observed on malt extract agar plates streaked with sample A_2 (effluent sample after chemical coagulation)

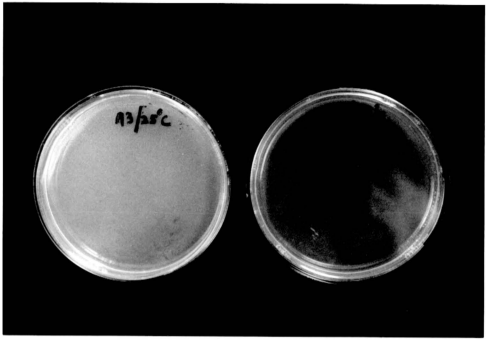


Photograph 5 : Microbiological growth observed on nutrient agar plates streaked with sample B_1 (effluent sample)

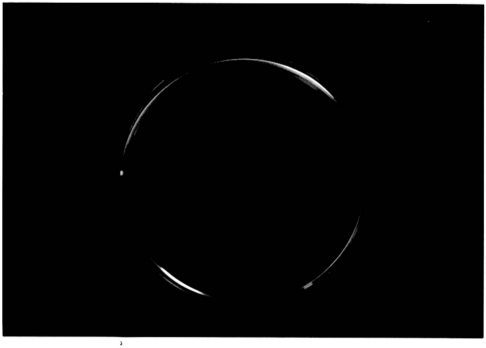


Photograph 6 : Microbiological growth observed on malt extract agar plates streaked with sample B_1 (effluent sample)

Photograph 7 : Microbiological growth observed on nutrient agar plates streaked with sample B_2 (effluent sample after chemical coagulation)

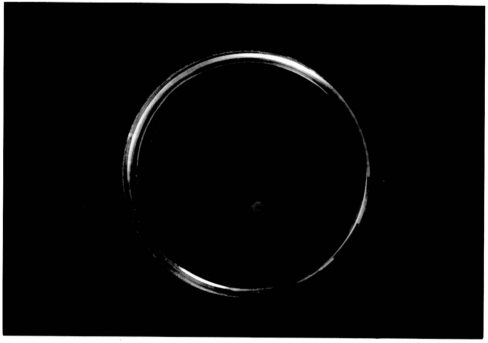


Photograph 8 : Nutrient agar plates streaked with sample A_3 (effluent sample after chemical coagulation and membrane treatment)

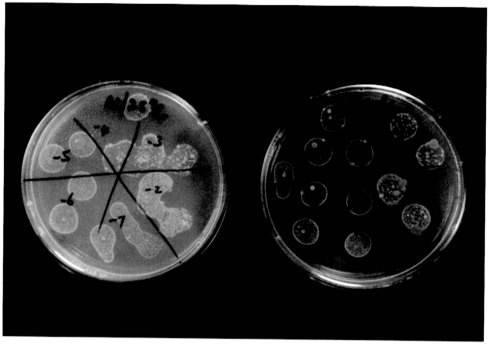


Photograph 9 : Malt extract agar plates streaked with sample A_3 (effluent sample after chemical coagulation and membrane treatment)

Photograph 10 : Nutrient agar plates streaked with sample B_3 (effluent sample after chemical coagulation and membrane treatment)

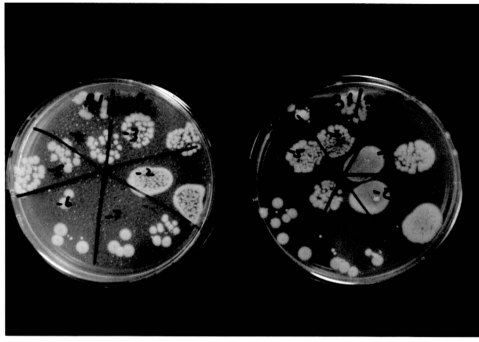


Photograph 11 : Malt extract agar plates streaked with sample B_3 (effluent sample after chemical coagulation and membrane treatment)

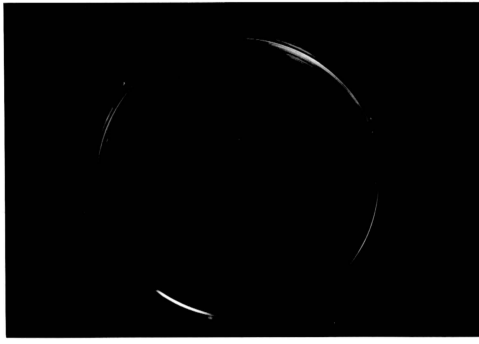


Photograph 12 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on nutrient agar plates streaked with sample A_1 (effluent sample)

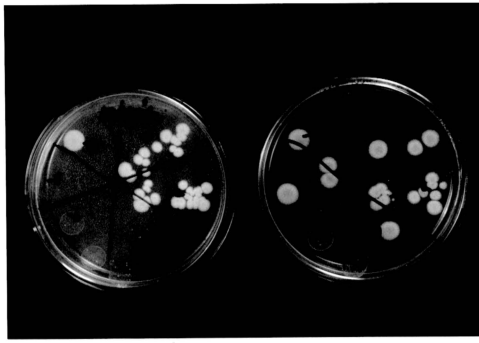
Photograph 13 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on malt extract agar plates streaked with sample A_1 (effluent sample)



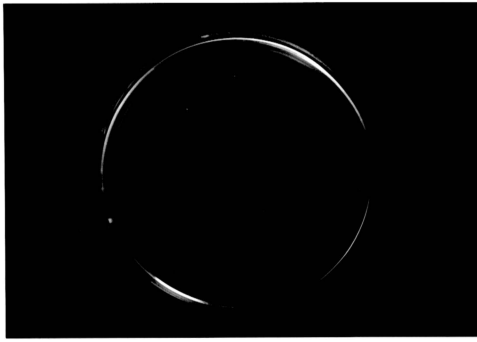
Photograph 14 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on nutrient agar plates streaked with sample B_1 (effluent sample)



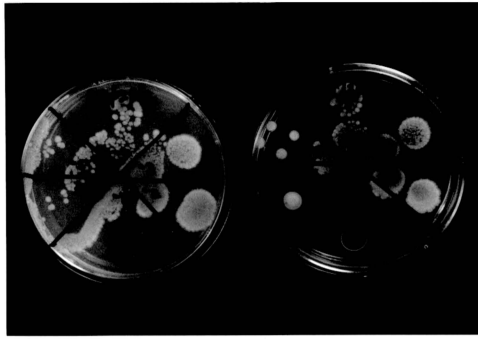
Photograph 15 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on malt extract agar plates streaked with sample B_1 (effluent sample)



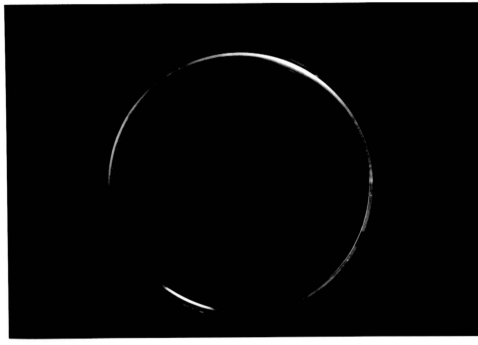
Photograph 16 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on nutrient agar plates streaked with sample A_2 (effluent sample after chemical coagulation)



Photograph 17 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on malt extract agar plates streaked with sample A_2 (effluent sample after chemical coagulation)

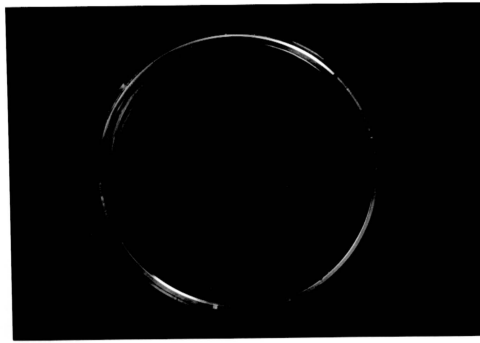


Photograph 18 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on nutrient agar plates streaked with sample B_2 (effluent sample after chemical coagulation)

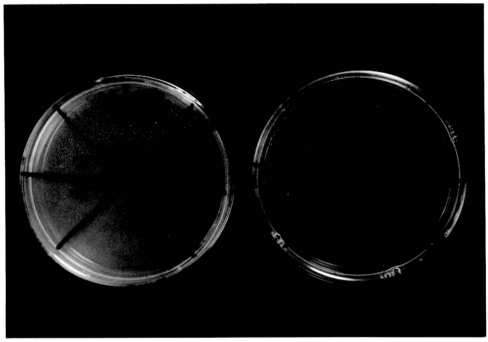


Photograph 19 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on malt extract agar plates streaked with sample B_2 (effluent sample chemical coagulation)

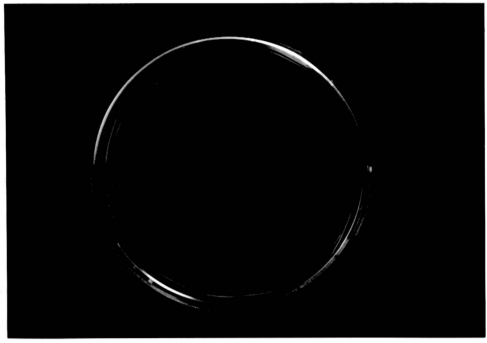
Photograph 20 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on nutrient agar plates streaked with sample A_3 (effluent sample after chemical coagulation and membrane treatment)



Photograph 21 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on malt extract agar plates streaked with sample A_3 (effluent sample after chemical coagulation and membrane treatment)



Photograph 22 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on nutrient agar plates streaked with sample B_3 (effluent sample after chemical coagulation and membrane treatment)



Photograph 23 : The Miles and Misra technique employed to determine the total viable count of microbiological growth observed on malt extract agar plates streaked with sample B_3 (effluent sample after chemical coagulation and membrane treatment)