ADVANCED OXIDATION COMBINED WITH A MEMBRANE BIO-REACTOR FOR LANDFILL LEACHATE TREATMENT

by

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Abstract

Treatment of landfill leachate is a challenge to the present day environmental scientist because direct impact of environmental protection costs is unaffordable to the developing countries. However intangible benefits of such treatment, creates a demand for better treatment techniques. Due to this environmental research is needed toward economic means of protecting the environment. The effort made in this research into the treatment of landfill leachate is a step towards this goal.

This work is a study of a biological process combined with a physico chemical method to treat landfill leachate. Use of membrane technology and advanced oxidation by ozonation are being proven to improve the efficiency of treatment of leachate.

This study focuses on comparing the efficiency of a Membrane bioreactor (MBR) in landfill leachate treatment at its standalone status supported by ammonia stripping as a pretreatment with continuous recirculation of ozonated effluent into the MBR. Efficiency of the process in terms of COD and BOD_5 are mainly studied. Molecular weight cutoff study (MWCO) is used to identify refractory and non refractory fractions of influent and effluent.

The systems pretreatment process, ammonia stripping was found to be 59% efficient. Also about 25% BOD_5 removal occurred during ammonia stripping reducing BOD_5/COD from 0.42 to 0.37. MBR organic loading was in the range of 2 to 3.5 kg/m^3/d. Food to microorganism ratio was in the range of 0.25 to 0.44 kg/kg.d of MLSS. MBR process was 71.5% efficient in COD removal and 93% efficient in BOD_5 removal. Also it showed a TKN removal efficiency of 35%. This efficiency was achieved with an average MLVSS/MLSS ratio of 0.55 in MBR.

DSVI of MBR sludge was 22 mL/g on average indicating sludge was difficult to settle. Also the drop in protein to carbohydrate ratio characterizes MBR sludge as difficult to settle.

Continuous recirculation of ozonated MBR effluent in 1:1 ratio with ammonia stripped leachate improved efficiency of MBR in terms of COD from 31% to 46%. Also TOC removal efficiency increased from 31% to 37%. The BOD_5 removal showed a drop from 93% to 83%. Therefore it can be concluded that recirculation of ozonated effluent causes improvement of MBR efficiency in a low magnitude.

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List of Abbreviations

A	Surface area of membrane, m^2
ADMI	American dye manufacturers institute
AOP	Advanced oxidation process
AOX	Absorbable organic halides
atm.	Atmospheric pressure
BOD_5	Biochemical oxygen demand (5 day)
cm.	Centimeter
cp	centipoises
COD	Chemical oxygen demand
CST	Capillary suction time
Deg. C , ^0C	Degree centigrade
ΔH	Heat of reaction
DI	De ionized
DO	Dissolved oxygen
DOC	Dissolved organic carbon
ΔP	Transmembrane pressure
DSVI	Diluted sludge volume index
EC_{50}	50% Effective concentration
EPS	Extra cellular polymeric substances
Eq.	Equation
F/M	Food to microorganism ratio
Fig.	Figure
g	Gram
h.	Hour
HRT	Hydraulic retention time
J	Flux, m/s
kDa	Kilo Dalton
Kg	Kilogram
kJ	Kilo Joule
k_m	Efficiency of cross flow effect
kPa	Kilo Pascal
L	Liter
LC_{50}	Lethal concentration for 50% kill
m	Meter
μ	Dynamic viscosity
m^3	Cubic meter
MBR	Membrane bio-reactor
MCRT	Mean cell residence time
μg	Microgram
mg	Milligram
min.	Minute
mins.	Minutes
mL	Milliliter
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
μm	Micrometer
mol.	Mole
MW	Molecular weight

MWCO	Molecular weight cut off
NBCOD	Non biodegradable COD
nm	Nanometer
OH^*	Hydroxyl radical
PVC	Polyvinyl Chloride
RBCOD	Readily biodegradable COD
R_m	Original membrane resistance
rpm	Revolutions per minute
s	Seconds
SBCOD	Slowly biodegradable COD
SMP	Soluble microbial products
SRT	Sludge retention time
SS	Suspended solids
SV_{30}	Sludge volume at 30 minutes settling
SVI	Sludge volume index
TCOD	Total COD
TKN	Total kjeldhal Nitrogen
TMP	Transmembrane pressure (kPa)
TOC	Total organic carbon
UF	Ultra filtration
V_p	Permeate volume, m^3
vs.	Versus
X_{TSS}	Total suspended solids

Chapter 1

Introduction

1.1 Background

Sanitary Landfill is considered to be the most common way of disposing urban solid wastes. It is the cheapest available method among other methods such as incineration and composting. An important problem associated with sanitary landfills is the production of leachates (Lema et al., 1988). Leachate is generally formed when rain water percolates through dumped waste and takes up the organic and inorganic products from both physical extraction and hydrolytic and fermentation processes. Generally, leachates contain high concentrations of soluble organic matter and inorganic ions (Wong and Mavinic, 1982 cited in Lema et al., 1988). Due to its high strength nature, direct discharge of leachate into the environment is not recommended taking into consideration the environmental impact as a result of it.

Presently, little attention is made to landfill leachate treatment and even less attention to treat sludge produced while treating leachate. Leachate Channeling (Combined treatment with domestic sewage, Recycling and lagooning), Biological Processes (Aerobic and Anaerobic) and Chemical/Physical Treatment (Chemical precipitation, Chemical oxidation, Adsorption, membrane technology and stripping of NH_3) are some of the leachate treatment methods. Leachate Channeling is reported to have created problems in the treatment process of domestic waste water treatment (Ahn et.al, 2002).

Under emerging cleaner production technologies, treatment methods for leachate and sludge produced need to be developed. Application of advanced oxidation methods (AOPs) are considered to enhance existing leachate treatment technologies. Advanced oxidation is the use of radicals, especially hydroxide radical to enhance oxidation in a treatment process. Hydroxide radical is one of the most powerful radicals used to treat water and wastewater (Zhou & Smith, 2002). As advanced oxidation processes are still in the development stage this study is intended to contribute to its development with respect to leachate and sludge treatment.

This study consists of two stages, namely biological leachate treatment and AOP. In the lab scale, the general treatment is simulated by Membrane bioreactor (MBR). MBR, though not widely used as a general treatment technique at present in developing countries, has future prospects of wide application as the cost of membranes are coming down. In this study, process optimization of MBR coupled with AOP is carried out to study effect of AOP on biological processes.

1.2 Objectives of the study

1. Different aspects which are considered in the combined treatment process of ammonia stripping, membrane bioreactor and post treatment with AOP are:

    1.1 Efficiency of the ammonia stripping process
    1.2 Efficiency of the MBR
    1.3 Ozonation of MBR treated effluent and recirculation

2. Understanding refractory nature of the leachate by molecular weight cutoff study
    2.1 On MBR influent and effluent
    2.2 On ozonated effluent mixed with ammonia stripped leachate as MBR influent and the corresponding MBR effluent

1.3 Scopes of the study

This study focuses on leachate treatment using mainly the membrane bio-reactor process and advanced oxidation process using ozonation.

1. A simulated leachate was used as influent in this experiment to represent medium aged landfill leachate.

2. Under ozonation study, performance of the optimized ozonation was monitored in a batch system and then proceeded to study continuous system.

Chapter 2

Literature Review

2.1 Introduction

Among several methods such as recycling, recovery, incineration and composting available for management of solid wastes, land-filling is still the most important method used for solid waste management. One of the byproducts of landfill is the leachate, which is formed due to chemical and biological reactions, which take place when rainwater is percolated through a landfill. Organic and inorganic compounds leach out from the waste in the landfill during this process is known as leachate. Unless managed and treated properly, leachate leads to adverse environmental impacts such as odor and groundwater contamination.

Various methods and technologies have been tested, applied and proposed to treat the landfill leachate. These methods range from simple methods such as recirculation through the landfill, to sophisticated ones such as combination of physical, chemical and biological processes. One difficulty in treatment is the temporal and spatial variation of the leachate characteristics. Therefore, selection of appropriate treatment is a challenging task. This study focuses on one of the cost effective ways of treatment of landfill leachate.

2.2 Composition and characteristics of landfill leachate

Leachate characteristics produced in a landfill is governed by following factors.

1. Composition of the waste being landfilled.
2. Climatic and hydrogeological conditions prevailing within the landfill area.
3. Age of the waste.
4. Leachate collection and management system used.

Two main characteristics of leachate are the volumetric flow rate and the composition. The flow rate from sanitary landfill change from site to site and seasonally at each site. The design of the tip, the climate (rainfall and evaporation) and the nature of the waste (moisture content and liquid entering the landfill) are the factors determining the flow rate (Lema et al, 1988).

Water percolating through landfill contains both organic and inorganic substances, released from the material deposited or as a result of biotic and abiotic reactions. These substances may be transported from the landfill through leachate, and could develop an environmental hazard. Different biological, chemical and physical processes taking place successively in a municipal landfill affect both the leachate and the gas production.

Leachate contains natural organic substances as suspended or colloidal particles, macro polymers or simple low molecular substances. Part of these organic substances remains as dissolved. Dissolved organic carbon (DOC) is the fraction of total organic carbon (TOC) passing through a 0.45 μm standard filter. The remainder caught by the filter is termed particulate organic matter. It can be assumed that DOC, besides the polymers, macromolecules and low molecular ions consists of 20 to 200 nm large colloidal particles or aggregates (Agren, 2003). DOC is refractory in nature.

Landfill leachate normally contains little suspended material. High concentrations of TOC mainly include humic substances which consist of Humic acids, Fulvic acid and Humins. Humic acids are the fraction of humic substances that is not soluble in water under acidic conditions ($pH < 2$) but is soluble at higher pH values. They can be extracted from soil by various reagents and which is insoluble in dilute acid. Humic acids are the major extractable component of soil humic substances. They are dark brown to black in color. Fulvic acids are the fraction of humic substances that is soluble in water under all pH conditions. They remain in solution after removal of humic acid by acidification. Fulvic acids are light yellow to yellow-brown in color.

Humins are the fraction of humic substances that is not soluble in water at any pH value and in alkali. Humins are black in color.

In addition to the large number of organic substances, municipal landfill leachates tend to contain large concentrations of salts, mainly NaCl and nitrogen (NH_4-N) along with heavy metals.

Leachate properties vary with the changing biological conditions in landfills. Generally, leachate characteristics could be divided into five phases according to the age of the landfill (Hayer & Stegman, 2003).

They are;

1. Aerobic phase
2. Acid phase
3. Intermediate methenogenic phase
4. Stabilized methenogenic phase
5. Final aerobic phase

Degradation starts under aerobic conditions at the beginning. Aerobic phase will be generally short due to limited amount of oxygen present inside the landfill. Oxygen is available in the upper layer of the landfill due to diffusion and rainwater. In this phase, proteins are degraded to amino acids and then into carbon dioxide, water, nitrates and sulphates. Carbohydrates are converted to carbon dioxide and water. Fats are hydrolysed to fatty acids and glycerol and are then further degraded into simple compounds through formation of volatile acids and alkalis. Cellulose, which is the main organic fraction of the waste, is degraded by the extracellular enzymes into glucose, which is subsequently converted to carbon dioxide and water by bacteria. This stage is exothermal, usually aerobic phase is short and no substantial leachate generation takes place.

Three different stages could be identified under anaerobic phase. First stage is the acid fermentation, which causes the decrease of pH. Acids disappear. High concentrations of volatile acids and inorganic ions such as Cl^-, $SO^{2-}{}_4$, Ca^{2+}, Mg^{2+}, Na^+ occur. Metals are more soluble at this stage. Leachate in this phase is characterized by high BOD_5 values usually greater than 10,000 mg/L , high BOD_5/ COD ratios generally greater than 0.7, acidic pH values from 5 to 6 and ammonia, 500-1,000 mg/L due to hydrolysis of proteinous compounds.

Second stage, intermediate anaerobic phase starts with slow growth of methenogenic bacteria, which may be inhibited by excess organic volatile acids, which are toxic to methenogenic bacteria. Methane concentration in the gas increases while the hydrogen, carbon dioxide and volatile fatty acids reduce. Further, the concentration of sulphate decreases due to biological reduction. Conversion of fatty acids increases the pH and alkalinity making Calcium, Iron, Manganese and heavy metals less soluble. These metals precipitate as sulphides. Ammonia is released without conversion in the anaerobic environment.

Third stage, anaerobic degradation phase is characterized by methenogenic fermentation by methenogenic bacteria. The pH range for methenogenic bacteria is 6 to 8. Low volatile acids and low total dissolved solids indicate that the solubilization of most of the organic components has decreased at this stage. Therefore the leachates of this stage are characterized by low BOD_5 values and low BOD_5/COD ratios.

According to Kruse (1994) cited in Heyer & Stegman (2003), acid, intermediate and methogenic phases could be characterized by BOD_5/COD ratio. The typical ratios of the three stages are presented in table 2.1 below.

Table 2.1 Landfill leachate age and biodegradability

Leachate Phase	**BOD_5/COD**
Acid	0.4
Intermediate	0.2 to 0.4
Methonogenic	0.2

Landfill management technology also affects the properties of leachate with respect to the age of the landfill. Present day younger landfill leachates have COD, BOD_5 and TOC levels lower than those found about ten years ago due to technical advancements in landfill management. Aerobic pretreated bottom layers and compaction in thin layers are examples of such improved landfill management methods, which accelerate the conversion of organics into gas phase.

In very old landfills where, more refractory organic carbons remain in the landfill wastes, a second aerobic phase may appear in the upper layer of the landfill. As methane production will be very low, air from the atmosphere starts diffusing into the landfill. This will give rise to development of aerobic zones in the landfill. Table 2.2 represents the constituents of municipal solid waste landfill leachate at different stages.

Table 2.2 Constituents in Municipal solid waste landfill leachates (Heyer & Stegman, 2003)

Parameter (mg/L except pH)	**Acid phase**	**Intermediate phase**	**Methenogenic phase**
pH	6.3-7.8	6.7-8.3	7-8.3
COD	950-40,000	700-28,000	460-8300
BOD_5	600-27,000	200-10,000	20-700
TOC	350-12,000	300-1500	150-1600
AOX	260-6,200	260- 3,900	195-3,500
NH_4-N	17-1,650	17-1,650	17-1,650
TKN	250-2,000	250-2,000	250-2,000

Young leachates are characterized by COD>10,000 mg/L, mainly due to volatile fatty acids, which are intermediate products of anaerobic degradation and by low nitrogen concentrations (<400 mg/L). Old leachates are characterized by high ammonia (>400 mg/L), high content of refractory compounds and low biodegradable organic fraction (Zamora et al, 2000).

Leachate quantity depends on rainfall precipitation, evaporation, surface run-off, infiltration and storage capacity. Generally about 18% of precipitation turns in to leachate. Water is consumed in the anaerobic biological degradation and lost due to gas production. With aging, this component reduces, thus increasing the volume of leachate produced.

2.3 Biodegradability of leachate

Different levels of biodegradability of leachate and their ranges are presented in table 2.3.

Table 2.3 Relative biodegradability of leachate

Biodegradability	**BOD/COD**	**COD/TOC**
Low	<0.5	<2
Medium	0.5-0.75	2-3
High	>0.75	>3

Biodegradable leachate can contain low molecular organic acids and alcohols, humic substances with high molecular weight, fulvic acid like materials with high molecular weight. The first group is made out of easily bio-degradable compounds, mainly fatty acids. In acidic leachate, the amount may be more than 90% of TOC. The second group consists of rather stable organics derived from cellulose and lignin. This group is present from 0.5% to 5% in the leachate. The third group contains compounds relatively rich in carboxylic and hydroxylic groups, which are predominant in methenogenic leachate and are difficult to degrade. Other than these organics, benzene, aminoacids, phenols and halogenated compounds, i.e. absorbable organic halides (AOX) may be detected in methanogenic leachates. Moreover, extremely high levels of ammoniacal nitrogen (500 to 3000 mg/L) can be observed too (Cossu et al., 2003).

Stabilized leachate has the following properties according to Baig & Liechti, 2001;

- COD < 2,000 mg/L
- Slightly alkaline pH
- Biodegradability (expressed as BOD_5 /COD) of 0.1

2.4 Treatment and disposal of landfill leachate

If the solid waste has very low biodegradability and toxicity, prevention of precipitation on the landfill would be a main treatment option. But, in general water input is essential for biodegradation of wastes to achieve high biostabilization.

Compared to municipal wastewater treatment, leachate treatment has a relatively limited history. Also, leachate treatment regulations vary from country to country. Some countries have strict regulations, some countries require simply collection of leachate and some countries have no definite requirements. Germany is one such country having a treated leachate requirement. The discharge limits are presented in table 2.4.

Table 2.4
Limiting concentrations for the discharge of treated leachate according to German Standards (Heyer and Stegman, 2003).

Parameter	**Limiting Concentration (mg/L)**	**Parameter**	**Limiting Concentration (mg/L)**
COD	200	Chromium	0.5
BOD_5	20	Chromium (VI)	0.1
Nitrogen, total (NH_4+NO_2+NO_3)	70	Nickel	1
Phosphorous, total	3	Lead	0.5
Hydrocarbons	10	Copper	0.5
Nitrite Nitrogen	2	Zinc	2
AOX	0.5	Cyanide	0.2
Mercury	0.05	Sulfide	1
Cadmium	0.1		

Leachate discharge standards of India are given in Table 2.5. According to Pollution Control Department of Thailand such standard is being prepaired.

COD, BOD_5, AOX and Nitrogen are the main parameters to be considered in leachate treatment. Variety of alternatives are available for partial and complete treatment of landfill leachate (Lema et al., 1988).

Table 2.5 Indian standards for discharging treated leachate
(Source www.cleantechindia.com)

Parameter	**Standard mode of disposal**		
	Inland surface water	**Public sewers**	**Land disposal**
Suspended solids mg/L, max	100	600	200
Dissolved solids (inorganic) mg/L, max	2100	2100	2100
pH	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
Ammonical nitrogen (as N) mg/L, max	50	50	-
TKN(as N) mg/L, max	300	350	100
Biochemical oxygen demand, mg/L, (3 days at 27^0 C) max	250	-	-
Chemical oxygen demand, mg/L, max	200	200	200
Arsenic (as As), mg/L, max	0.01	0.01	-
Mercury (as Hg), mg/L, max	0.1	0.1	-
Lead (as Pb), mg/L max	2.0	1.0	-
Cadmium (as Cd), mg/L, max	2.0	1.0	-
Total Chromium (as Cr) mg/L, max	2.0	2.0	-
Copper (as Cu), mg/L, max	3.0	3.0	-
Zinc (as Zn), mg/L, max	5.0	15	
Nickel (as Ni), mg/L, max	3.0	3.0	-
Cyanide (as CN), mg/L, max	0.2	2.0	0.2
Chloride (as Cl), mg/L max.	1,000	1,000	600
Flouride (as F), mg/L, max	2.0	15	-
Phenolic compounds (as C_6H_5OH) mg/L, max	1.0	5.0	-

Few treatment options are:

- Leachate channeling
    - Combined treatment with domestic wastewater
    - Recycling
    - Lagooning with recycling
- Biological processes
    - Aerobic treatment
    - Anaerobic treatment
- Chemical / Physical treatment
    - Chemical precipitation
    - Chemical oxidation
    - Adsorption on activated carbon
    - Reverse osmosis
    - Ammonia stripping

Addition of leachate into municipal wastewater treatment plant is a option for leachate treatment but may initiate new problems such as high effluent flows and high sludge production which need careful design and operation of the treatment plant. Although, co-treatment of landfill leachate with municipal waster water treatment plant is a viable option, stringent effluent discharge requirements demand the need to separate treatment of leachate to meet the standards.

2.4.1 Biological treatment of leachate

Biological treatment is the most common practice for the leachate treatment, which is relatively economical when compared with physico chemical methods. It could be aerobic or anaerobic treatment. Biological treatment of leachate is effective in COD removal even in low biodegradable leachate of BOD_5: COD <0.2 (Heyer & Stegman, 2003).

2.4.1.1 Anaerobic biological treatment

Parts of the landfill itself could be used as an anaerobic biological reactor. Up-flow anaerobic sludge blanket process or anaerobic filter could be used. Anaerobic treatment step is economical due to low energy requirement and no oxygen requirement.

Anaerobic treatment reduces BOD and COD to a BOD: COD ratio greater than 0.3, which has medium biodegradability suitable for aerobic treatment. An important feature of anaerobic treatment is the possibility of using the CH_4 generated for external uses.

2.4.1.2 Aerobic biological treatment

Aerated lagoons, activated sludge, rotating biological contactors or trickling filters could be used for this purpose. Retention time in activated sludge process is shorter than that for aerated lagoons, reason being the sludge control and recirculation adopted in activated sludge process.

A problem associated with aerobic treatment is that the C: N ratio expressed as BOD: N ratio in methenogenic leachates may be 100:100 while the optimum suited ratio for bacteria is 100:5. Due to excess nitrogen, the biological process may not run reliably producing unacceptable concentrations of ammonia (Fletcher and Ashbee, 1994).

Besides BOD_5 reduction, denitrification of ammonium is an important process in activated sludge plants. The pH of old leachate could be in the range of 8 to 8.3. When aerated, the pH could rise to 9 or higher. Under these circumstances the ammonia equilibrium shifts from ammonium to free ammonia affecting the growth of denitrification bacteria through inhibition. During the same time, conversion of ammonium to nitrate reduces pH. Therefore pH control is essential in getting low effluent ammonium levels.

After biological treatment, the organic load consists of humic acids and halogenated organic constituents. Humic acid is a mixture of partially decomposed or transformed organic materials. A substantial fraction of the humic acid is in carboxylic acid functional groups. It is complex refractive mixture of aromatic organic acids. Humic acid contains sulphur, nitrogen and phosphorous in varying amounts. It also contains metals such as Ca, Mg, Cu, Zn etc.which could be chelated in some undefined way. Humic acid can be broken down into two groups based on the polarity and size of the individual compounds. The smaller the polar fraction, generally termed fulvic acid and the larger the no-polar fraction, generally termed humic acid.

Biological oxygen demand (BOD) and chemical oxygen demand (COD) are the parameters traditionally used to measure concentrations of organic substances in leachates. Especially, BOD and BOD/COD ratio give valuable information regarding the relative difficulty to degrade the organic substances, the supply of carbon source in dentrification, or the maturity phase dominating the landfill.

2.4.2 Physico-chemical Treatment

Old leachates are characterized by ammonia, refractory substances and low biodegradable organic fraction (BOD_5/COD in the range of 0.1). Therefore, old leachates cannot be treated to required standards by biological processes alone. Effective removal of these substances could be achieved by more sophisticated methods such as advanced oxidation, adsorption with activated carbon or combination of these with conventional physico-chemical methods (Zamora et al., 2000).

2.4.2.1 Ammonia stripping

There are several methods available for nitrogen removal in leachate. One method is biological process-nitrification and denitrification. The other is physico-chemical treatment such as ion exchange, reverse osmosis, electrodialysis, break-point chlorination and stripping. Ammonia stripping is a cost effective means of nitrogen removal instead of nitrification-denitrification step. In leachates, the ammonia level frequently exceeds 1000 mg/L. This is around 100 times greater than concentrations found in sewage. Ammonia is mainly produced during the methanogenic stage of degradation, due to breakdown of proteins to amino acids and subsequent de-amination releasing ammonium ion. Very little of this ammonium ion is converted to ammonia. Leachate has high ammonia concentration and low BOD: N ratio. Chlorination is not preferred for ammonia removal as it can lead to production of chloramines, which are carcinogenic. When large concentration of ammonia is present, it is economical to strip it than transforming into nitrate.

Ammonia has a low Henry’s constant, which means it is highly soluble, thus large quantity of air is required to desorb it from liquid to gas phase. Also desorption is difficult at low temperatures. Ammonia is normally present in water as soluble ammonium ion, NH_4^+. This has to be converted to gaseous ammonia molecule for stripping to take place. This conversion is accomplished by raising pH to around 11 to 12 usually by adding lime or NaOH.

$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3 \qquad \text{Eq. 2.1}$$

The quantity of alkali required depends not only on ammonia concentration but also on the carbon dioxide, alkalinity, calcium, magnesium, iron, manganese and organic acid levels. This pH correction adds to the cost of treatment. But, it also helps to remove substantial portion of heavy metals and some of the organic load. Therefore, it is beneficial in terms of overall treatment process.

In atmosphere, ammonia is present around 5 to 15 $\mu g/m^3$ through natural emissions. Toxic level of ammonia is 1700 mg/m^3. Odor threshold is 35 mg/ m^3. Ammonia could be trapped using sulfuric or phosphoric acid in a scrubber, offering the potential for use as a fertilizer. Alternatively, the ammonia may be incinerated in combination with landfill gas. It has been found that the liquid surface area and turbulence influence the ammonia removal rate (Smith & Arab, 1988 cited in Fletcher and Ashbee, 1994). Table 2.6 summarises the studies done on ammonia stripping for landfill leachate.

Table 2.6 Ammonia stripping of landfill leachates. (Fletcher and Ashbee, 1994)

Process Stream	Influent Ammonia (mg/L)	Stripping process	% Ammonia removal	Process detail	Reference
Landfill leachate	100-200	Diffuse air	90-95	Pilot scale	Damhaug,1981
Landfill leachate	200-1,000	Diffuse air	50	Lab scale	Robinson,1981

2.4.2.2 Chemical oxidation

Biologically stabilized landfill leachate requires further removal of organic substances before final discharge. Chemical oxidation is a convenient method for the removal of organics. But it is not efficient in removal of ammonia nitrogen. Chemical oxidation can make refractory organics capable of undergoing subsequent biological treatment. During chemical oxidation organic compounds can be converted to simple final products such as water and carbon dioxide. Various oxidants such as hydrogen peroxide, potassium permanganate, oxygen, ozone and chlorine can be used. Chlorine has the drawback of producing toxic products. Ability to oxidize depends on the oxidation potential of the oxidant. Oxidation potentials of various oxidants are presented in table 2.7.

Table 2.7 Oxidation potential of some oxidants (Fraser & Sims, 1984 cited in Cossu et al, 2003)

Oxidant	Reactions	Oxidation potential (volt)
Hydroxyl radical	$OH^{\cdot} + H^{+}+e=H_2O$	2.80
Ozone	$O_3+2H^{+}+2e=H_2O+O_2$	2.07
Hydrogen peroxide	$H_2O_2+2H^{+}+2e=2H_2O$	1.77
Permanganate	$MnO_4^{-} + 8H^{+}+5e= Mn^{2+}+4H_2O$	1.52
Chlorine dioxide	$ClO_2+e= Cl^{-} + O_2$	1.50
Chlorine gas	$Cl_2 + 2e= 2Cl^{-}$	1.36

Most reactive oxidant is the OH radical on which most of the advanced ozonation processes are based. Following oxidation methods have been applied to leachate treatment.

- Wet oxidation
- Hydrogen peroxide
- UV
- Ozonation

a. Wet oxidation

Wet oxidation is the process of using oxygen as the oxidant. The reaction occurs at high temperature (175-320^0 C) and at high pressure (20-200 atm.) with 1-2 hours retention time. Oxygen is added as pressurized oxygen or pure oxygen. This treatment is suitable for treatment of leachate with high COD in the range of 10,000 to 20,000 mg/L (Cossu et al., 2003).

b. Hydrogen peroxide

Hydrogen peroxide can easily oxidize refractory organics, such as humic substances in the presence of a catalyst. During the reaction, OH radicals which are of oxidation potential higher than hydrogen peroxide alone (Table 2.7) are formed. Iron salts (Fentons reagent) and UV radiation are two possible catalysts. On the other hand hydrogen peroxide can act as a catalyst for ozonation.

Production of radicals is as follows;

$$H_2O_2+ \text{uv-radiation} \rightarrow 2\ OH^{*} \qquad \text{Eq. 2.2}$$

Fast reaction of OH^{*} can be written as follows.

$$OH^{*} + \text{organic substance} + \text{UV radiation} \rightarrow H_2O + CO_2 + \text{organic residue} \qquad \text{Eq. 2.3}$$

The reaction rate can be reduced by radical scavengers such as such as acetate, carbonate and bicarbonate. Therefore, the competing compounds need to be kept at low level. As carbonate concentration is reduced at low pH, a value of around 3 is recommended.

c. UV radiation

UV radiation has been widely used as a microorganism reduction step since mid seventies. The process usually involves the use of low pressure UV lamps.

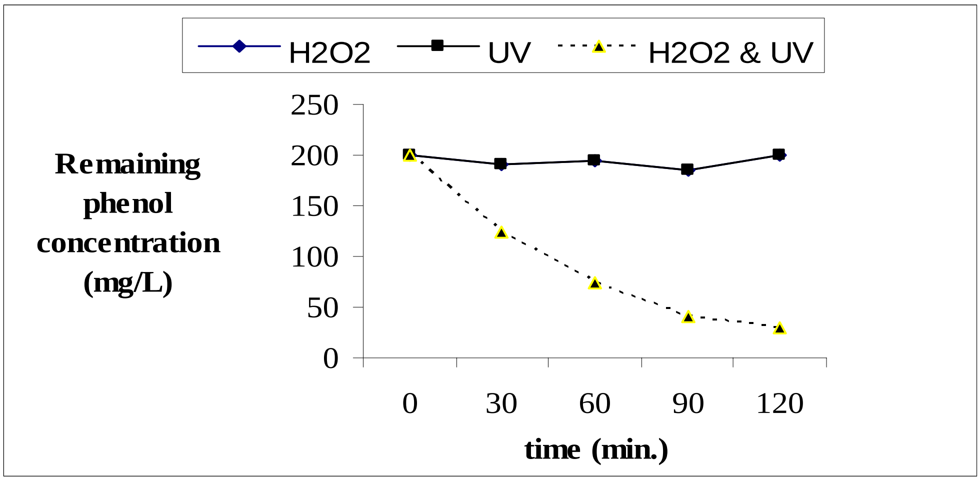


Figure 2.1 Treatment of phenol with H_2O_2 alone and combined with UV, (Drouiche et al., 2001)

Drouiche et al., 2001 reported that UV radiation alone cannot contribute much to oxidation of organic compounds. Results of treatment of phenolic solution with UV radiation and H_2O_2 are given in figure 2.1 above. According to the results a contact time of 120 minutes of UV alone and H_2O_2 alone is not capable of degrading a phenol solution. But a remarkable change in phenol concentration occurs when treated with combined H_2O_2 and UV. The difference is due to formation of OH^* by photolysis of H_2O_2 by UV radiation.

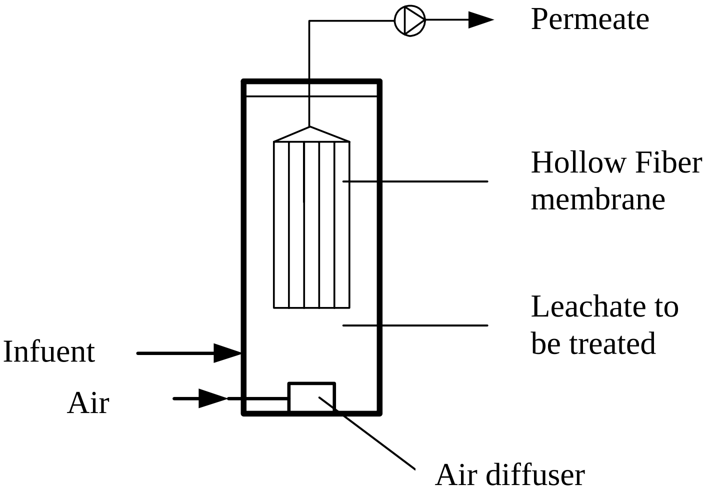


Figure 2.2 Submerged membrane bioreactor with hollow fiber membrane

2.5 Membrane bioreactor process

Membrane bioreactor, an innovative technology, has the capability to combine biological process and physical separation into a single unit. Figure 2.1 presents basic detail of membrane bioreactor. Membranes have been finding wide application in water and waste water treatment since early 1960s. Membrane filtration can be defined as a separation process that uses semipermeable membrane dividing the feed stream into two portions, a permeate that contains the material passing through the membranes and a retentate consisting of the species being left behind. (Zhou et al, 2002) Special quality of membrane is semipermeability. Initial studies of membrane reactors involved cross flow modules, which has disadvantage of requirement of high speed pumping devices. These pumps impose high shear stress on the flocs. Submerged membrane bioreactor system in which a membrane module is directly immersed in an aeration tank is becoming wide spread because it has no such problems as cross flow units (Kim & Lee, 2003). One of the limitations of the membrane bioreactor is the membrane fouling problem and associated increased operation cost of the system.

2.5.1 Advantages of membrane bioreactor

Membrane bioreactor has several advantages over the conventional activated sludge process. Main advantages are better effluent quality due to prevention of leakage of undecomposed polymer substances, small size of the plant and less sludge production, disinfection and odor control.

These advantages make MBR superior with respect to disadvantages in conventional activated sludge process such as high sludge production, requirement of large areas. Parameters affecting conventional activated sludge process are feed concentration, sludge retention time (SRT), hydraulic retention time (HRT), biomass concentration in the aeration tank, organic loading, food to micro organism ratio, sludge wastage rate and sludge settling characteristics in the settling tank. An increase of the biomass concentration will increase the degradation rate and reduce the area needed. But high MLSS in the aeration tank will cause settling problems because the settling properties will be poor at high sludge concentrations. Also a disadvantage of the secondary settling tank is that its separation ability depends on the operational conditions of the aeration tank. Therefore the performance enhancement of conventional activated sludge process could be achieved though new method such as membrane separation which does not use sedimentation (Setiadi and Fairus, 2003).

Membrane process eliminates settlement problems associated with conventional activated sludge process such as nutrient deficiency as solids and colloids are totally removed through the membrane process. This makes the system operation easy. The membrane process totally eliminates the suspended matter in permeate. In MBR, the SRT can be independently controlled from hydraulic retention time. Therefore, a very long SRT could be achieved resulting in the complete retention of slow growing microorganisms such as nitrifying bacteria. Volumetric capacity is high in MBR as high sludge concentration could be maintained independent of settling properties. HRT as low as 2 hours could also be achieved. Fluctuations in volumetric loading have no effect on effluent quality. Table 2.8 presents a comparison between the conventional activated sludge process and MBR.

Table 2.8 Comparison of MBR and conventional Activated Sludge Process (Visvanathan et al., 2000).

Characteristic	MBR	Conventional activated sludge process	Reference
Sludge concentration	25 to 30 kg/m^3	4 to 6 kg/m^3	Yamamoto & Win, 1991
Floc size of sludge	Very much smaller than 100 μm and concentrated within small range	0.5 to 1000 μm	Zhang et al., 1997
Nitrification activity gNH_4-N /Kg MLSS.h	2.28	0.95	Zhang et al., 1997

Also, MBR has high rate of decomposition of biodegradable polymer substances. The dissolved organic substances with low molecular weights, which cannot be eliminated by membrane separation alone can be gasified or used to produce polymers by bacteria creating high biomass concentrations in MBR process.

2.5.2 Membrane bioreactor operation

Membrane fouling is one of the problems associated with the MBR process Membrane fouling is affected by hydraulic conditions such as cross flow velocity and aeration intensity as well as nature of the microbial flocs.

Membrane bio-reactor is a combination of biological process and membrane separation. Therefore, it is a complex process. Related parameters for optimization of MBR process are solids concentration, sludge age, hydraulic retention time, flux, material cost and the energy cost. Treatment and disposal of waste sludge is also an important parameter.

Dewatering of MBR sludge is difficult when compared with conventional activated sludge process due to high organic matter content and excess production of extra cellular polymers (Parameshwaran, 1977 cited in Visvanathan, et al., 2000).

Understanding the relationship between operating parameters, biological performances (degradation efficiency, intermediate products etc.) and filtration efficiency is important in optimizing a membrane bioreactor. Membrane bioreactor is attractive in achieving long solids retention time as needed by nitrifying bacteria and physical retention required for biological degradation of pollutants (Chen et al., 2003).

Although, the increase of sludge concentration helps to enhance biological activity, increase of sludge viscosity disturbs the permeate flux. In addition, gas transfer efficiency will drop needing more energy for aeration.

Permeate flux of the membrane filtration is also influenced by raw materials of the membrane, pore size and operational conditions such as the trans membrane pressure, the liquid turbulence and the physical properties of the mixed liquor being filtered.

Submerged Hollow fiber membrane of 0.1 μm has reported COD removal of more than 90%, Nitrate removal above 80% and denitrification efficiency ranging from 20 to 60%. During steady operation food to microorganism ratio, F/M was 0.1 kg COD/kg MLSS.d. Moreover, the critical organic loading rate was estimated 3 to 4 kgCOD/m^3.d. (Visvanathan et al., 2000).

2.5.3 Activated sludge process within the membrane bioreactor

Activated sludge process is the most widely used biological process in wastewater treatment. It was discovered in 1914 by Ardern and Lockett, and commercialized in 1920 by John and Atwood as a continuous process (Urbain, et al., 1998).

2.5.3.1 Sludge load

Biological sludge contains 0.25 to 12% solids depending on the wastewater process (Erdincler and Vesilind, 2000). Sludge loading rates for activated sludge processes and mean cell residence time (MCRT) are shown in the table 2.9. Sludge load is high when greater than 0.3 kg BOD/ kg MLSS.d. Floc type can be open or compact. In open floc, water can flow through the flocs. Compact flocs are brown in color and contain bacteria compact close together and settle faster. Compact flocs occur when sludge load is lower than 0.3 kg BOD/ kg MLSS.d.

Table 2.9 Typical process loading ranges for the activated sludge process. Thiel (2002)

Loading range	Volumetric loading kg BOD/m^3	MCRT, d	F:M , kg/kg.d
High rate	1.6-16.0	1-3	0.5 – 1.5
Conventional	0.32-0.64	5-15	0.2 – 0.5
Low rate	0.16-0.40	20-30	0.05 –0.15

2.5.3.2 Turbulence

Also there is a relationship with turbulence caused by air with the compact flocs. Turbulence caused by aeration can reduce the production of compact flocs.

2.5.3.3 Firm and weak flocs

In firm flocs the boundary between the floc and the surrounding liquid is clear which is not clear in case of weak flocs which can be easily damaged.

Also small load < 0.025 kg BOD/ kg MLSS.day could lead to floc disintegration due to consumption of polymeric capsules around the cells in the floc. Extreme turbulence in the aeration tank too can lead to such floc reduction.

Floc mainly consists of living and dead cells. Free living cells refer to the cells that are not bound to the floc but are loose in the water phase. Free cells become more if the sludge load exceeds the limit of 0.3 to 0.4 kg BOD/kg MLSS.day. The presence of many free cells at a low sludge load is an indication of lack of oxygen or the presence of toxic components in the effluent.

Floc formation in activated sludge avoids bacteria being eaten by protozoa and being washed out. Protozoa and Metazoa are mainly fed by free bacterial cells or present at the edges of the flocs. Some protozoa consume sludge flocs or other protozoa.

In contrast to protozoa, metazoa are multi-cellular micro organisms, meaning ‘higher’ organisms with varying sizes of 100μm to 2 cm. Most metazoa are fed on free living bacteria or small floc particles. Some specie consumes whole sludge flocs. Rotifers, Nematodes, Worms and Tardigrades are metazoan groups that could be present in activated sludge. They are observed at sludge loading levels lower than 0.15 kg BOD/ kg MLSS.d. Out of them, the worms which were observed in the reactor can consume sludge flocs or particles of flocs. A worm boom is connected with reduction in sludge production. Sludges with worms occur at sludge loads of 0.1 kg BOD/kg MLSS.d. and in which the influent is pre-settled (Eikelboom, 2000). Worms cannot survive long periods in days without oxygen. Therefore low oxygen supply could control worms.

According to Hanel (1988) protozoa and metazoa in general have a positive role in activated sludge. The more species are there, the greater is the chance that even the more refractory substances will be utilized by the sludge and decomposed, or else deposited in the form of non biodegradable matter within the organisms, for example in the fatty tissues of the metazoa.

Protozoa and other higher life forms are usually aerobic and bacteriovorous (eat bacteria). They constitute about 5% of the activated sludge biomass. These organisms perform several important functions in activated sludge. Most important of which is the removal of nonflocculated bacteria from wastewater through their feeding activities yielding a clarified effluent. Additionally these contribute to biomass flocculation through fecal pellets and mucus (Jenkins et al., 1993).

Sludge age also play an important role in sludge concentration and microorganisms. Only microorganisms with generation time less than the sludge age can be maintained in the sludge. Therefore sludge wasting is an efficient way of controlling microorganisms in activated sludge. Nematodes are generally observed only in higher MCRT systems, while tardigrades and annelids appear to occur only in nitrifying activated sludge systems, probably due to their susceptibility to ammonia toxicity.

Optimum activated sludge performance occurs when there is a balance between free swimming and attached ciliates and rotifers. An over abundance of flagellates, amoebae or free swimming ciliates is an indication of high F/M (low MCRT) and over abundance of attached ciliates, rotifers and other higher life forms, especially nematodes are an indication of low F/M (high MCRT). Operational conditions of activated sludge process and observed microorganism types are shown in Table 2.10.

Table 2.10 Organic loading of activated sludge and predominant higher life forms observed (Jenkins et al., 1993)

Condition	Predominant groups
High F/M; low MCRT	Flagellates, amoebae, and small free swimming ciliates
Moderate F/M; average MCRT	Good diversity of organisms dominated by free swimming and stalked ciliates
Low F/M, high MCRT	Stalked ciliates, rotifers and higher invertebrates, specially nematodes

Effects of low dissolved oxygen (DO) according to Thiel (2002) are as follows.

- Presence of filamentous bacteria
  Due to low DO, growth of filamentous bacteria occurs. It affects the settleability of activated sludge. Filamentous bacteria are needed to make flocs stronger by making long strings or filaments out of bacteria sitting end to end. Filamentous bacteria had to be in balance. If it is over grown and SVI become > 150 mL/g sludge will bulk making poor settling characteristics. Filamentous bacteria are also known to cause foaming in activated sludge.
- Turbid effluent
- Dark gray or black activated sludge

In summary, microorganisms can be used as bio indicators for operation of activated sludge process.

2.5.3.4 Effect of toxicity

Toxicity starts affecting protozoa and metazoa, the higher forms of microbes in activated sludge first. It causes blooming of small free swimming ciliates. This is an indication of activated sludge breakup and the production of large number of dispersed bacteria (turbidity), which are food source for free swimming ciliates. Death of these protozoa causes white foams containing protozoa and protozoan fragments due to cell lysis and release of cell contents. Therefore high level of foaming in MBR could be attributed to toxicity.

2.5.4 Sludge characteristics

Sludge characteristics of MBR MLSS can be evaluated in terms of

1. Viscosity
2. MLSS and MLVSS
3. Capillary suction time (CST)
4. Sludge volume index (SVI) or Diluted sludge volume index (DSVI)
5. EPS analysis

Very thin activated sludge behaves very close to water (Newtonian behavior). However, with the increase of solids concentration, activated sludge exhibits non-Newtonian flow character. Activated sludge has been identified as either a plastic or a pseudoplastic non Newtonian fluid (Sanin, 2002). The contribution to non Newtonian behavior is believed to originate from colloidal properties of the sludge. Viscosity of the dispersion medium of activated sludge is an important rheological property among other properties such as particle concentration, particle size and shape, particle-particle and particle-dispersion medium interactions. Viscosity of sludge increases with the increase of solids concentration. According to Sanin (2002), increase of apparent viscosity with solids concentration follows an exponential pattern, which explains stronger non Newtonian behavior with increasing solids concentration. Viscosity of activated sludge also found to be lowest when pH 5.5 which is a value close to the iso-electric point of bacteria and increasing with the increase of pH.

Capillary suction time determines the rate of water release from sludge. It provides a quantitative measure in terms of time in seconds. It’s a measure of sludge dewaterability.

SVI is the volume of 1 g of sludge after 30 minutes of settling. SVI is measured by placing mixed liquor sample in 1 to 2 L capacity measuring cylinder and measuring the settled volume after 30 minutes and the corresponding sample MLSS concentration. A value of 100 mL/g is a good settling sludge (Metcalf and Eddy, 2003). SVI > 150 are associated with filamentous growth. In case of sludge is not settling, dilution of sludge need to be done to make the 30 minute settling volume (SV_{30}) 200 mL /L or less. In this case the value is reported as DSVI. (Jenkins et al., 1993). DSVI is calculated using equation 2.4, where SS stands for suspended solids and n stands for dilution factor.

$$\text{DVSI (mg/L)} = \frac{SV_{30}\text{ (mL/L)}}{\text{SS (g/L)}} \cdot n \qquad \text{Eq. 2.4}$$

Extracellular polymeric substances (EPS) are a key component of aggregation of microorganisms in biofilm flocs and sludge. EPS consists of polysaccharides, proteins, nuclic acids, lipids and other biological macromolecules. EPS provide highly hydrated gel matrix in which microbes can establish. Protein and carbohydrate are the main components found in EPS. It is reported that BOD: N: P ratio has an effect on hydrophobicity, surface charge, bound water and EPS composition of microbial flocs (Bura et al., 1998). Polymers are high molecular mass and high viscosity substances and they act as glues in holding activated sludge particles together. It has been found that EPS affect the viscosity of sludge (Sanin, 2002).

2.5.5 Membrane fouling

Membrane fouling control is a major issue for an economically feasible MBR operation. Soluble microbial products (SMP) play an important role in membrane fouling and effluent quality in addition to the mixed liquor suspended solids. SMP is produced by cell lysis and tends to accumulate on membrane surface causing membrane fouling. F/M ratio and Sludge retention time are found to be critical factors in controlling SMP concentration in a reactor (Lee et al., 2002). SMP contains refractory organic matters. Higher the SMP concentration, faster is the membrane fouling. SMP generated from cell lysis tends to accumulate on membrane surface causing membrane fouling.

Membrane fouling can be modeled by following equations;

$$J = \frac{\Delta P}{\mu R} \qquad \text{Eq. 2.5}$$

$$R = R_m + m\,a \qquad \text{Eq. 2.6}$$

$$m = k_m \frac{V_p X_{TSS}}{A} \qquad \text{Eq. 2.7}$$

Where, J = Flux, m/s

ΔP = Trans-membrane pressure, kPa

μ = Permeate viscosity, Pa.s

R = Total resistance of fouled membrane, 1/m

R_m = Original membrane resistance, 1/m

m = Accumulated mass on membrane surface, kg/m^2

a = Specific resistance, m/kg

k_m = efficiency of cross flow effect

A = Surface area of membrane

X_{TSS}= Total suspendend solids

V_p = Permeate volume, m^3

The term k_m ranging from 0 to 1 is introduced to represent the cross flow filtration where for dead end filtration, $k_m = 1$. In cross flow filtration k_m represents not all particles are deposited onto the membrane surface.

The resistance caused by accumulated substances is due to pore blocking, adsorption, gel layer formation and concentration polarization. During filtration particles accumulate near the pores forming a concentrated layer increasing the resistance for mass transfer. This is termed concentration polarization. Particularly, when a solution contains protein such layer can be of very high concentration forming a gel layer. Adsorption can occur on the membrane surface as well as inside the pores. As the shape of protein depend on pH, is found that fouling is minimised at pH value corresponding to the isoelectric point of the protein, i.e. at the point at which the protein is electrically neutral.

Membrane cleaning is the method available to remove foulants from a membrane. Cleaning can be done hydraulically and chemically. Hydraulic cleaning is done by back flushing and chemical cleaning of the membrane by means of disinfecting by NaOCl and using sodium hydroxide (Mulder, 1996).

According to Aim and Semmens (2002), additional resistance in a membrane can be created by formation of a biofilm on the membrane. It is reported that backwashing is an effective means of removal of this biofilm.

2.6 Ozonation

Main uses of ozone in wastewater treatment are disinfection and oxidation. Oxidation by ozonation contributes to odor control, decoloration and elimination of micropollutants. Even though ozone dissolves in water, it is highly unstable in water and undergoes reactions with water. The solubility of ozone in water at different temperatures is given in Table 2.11.

Table 2.11 -Solubility of ozone in water

Temperature (^{0} C)	**Solubility (kg/m^3)**
0	1.09
10	0.78
20	0.57
30	0.40
40	0.27
50	0.19
60	0.14

The unique feature of ozone is its decomposition into OH radicals (OH^*) which are the strongest oxidant in water. Disinfection occurs dominantly by ozone. Oxidation process occurs through both ozone and OH radicals. OH radical reaction is important in oxidization of ozone resistant compounds.

Ozone is a selective oxidant. It reacts fast with many dissolved compounds in water. For ozone reactions more than 500 rate constants have been measured for OH radical reactions out of a database of few thousand rate constants (Gunten, 2003). Disinfection and ozonation could be achieved simultaneously by ozone and ozone needs to be transformed to OH radicals for oxidation of ozone resistant compounds.

The oxidation potential of ozone alone is high enough for direct oxidation of organic materials. An initiator such as H_2O_2 can accelerate the formation of OH radicals. Control of radical scavengers is important even in this stage. Generally, the consumption of ozone is about 2.3-3 g O_3/g COD removed (Cossu et al., 2003).

Disadvantages of ozonation process are

- High cost for reagents
- High energy consumption
- Low reduction of inorganic compounds such as ammoniacal nitrogen.

Ozone is an irritating pale blue gas, heavier than air, very reactive and unstable.
Formation of ozone is an endothermic process. Ozone is thermodynamically unstable and instantly converts back to oxygen as shown in the following equation.

$$3O_2 \rightleftharpoons 2O_3 \qquad \Delta H \text{ at 1 atm} = +284.5 \text{ KJ.mol}^{-1} \qquad \text{Eq 2.8}$$

It cannot be stored and transported, so it has to be produced ‘in situ’. Ozone is toxic and explosive even at low concentrations. Ozone is about 14 times soluble in water.
Ozone molecule is considered to have the resonant structure as given in figure 2.3.

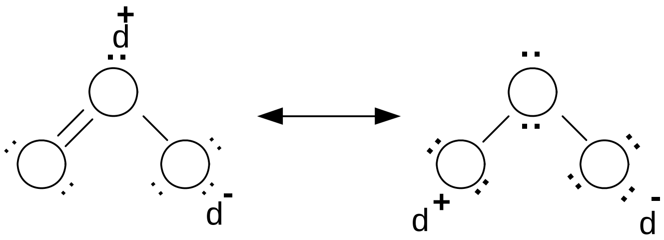


Figure 2.3 Structure of ozone

In aqueous solutions, ozone may act on various compounds (M) in two ways. (Figure 2.4)

1. Direct reaction with molecular ozone.
2. Indirect reaction with the radical species, which are formed when ozone decomposes in water.

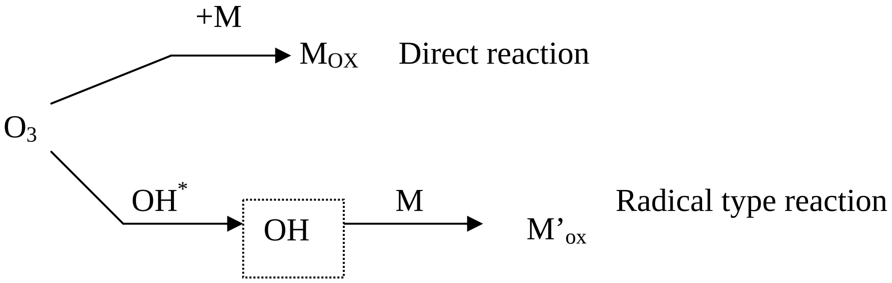


Figure 2.4 Reactions in ozonation process

Stability of dissolved ozone is affected by pH, UV light, ozone concentration and the concentration of radical scavengers. The OH radicals formed during the reaction of ozone with water could be scavenged by bicarbonate and organic solutes or may react further with ozone to yield more free radicals. The decomposition rate, measured in the presence of excess radical scavengers, which prevent secondary reactions is expressed by a pseudo first order kinetic equation:

$$-\left(\frac{d[O_3]}{dt}\right)_{pH} = k' [O_3] \qquad \text{Eq. 2.9}$$

Where, k' is first order rate constant for a given pH value.
The overall equation can be given as following.

$$-\left(\frac{d[O_3]}{dt}\right)_{pH} = k [O_3] [OH^*] \qquad \text{Eq. 2.10}$$

Where $k = k'/[OH^*]$

Ozonation processes are generally designed for process time lasting in the range of 10 minutes. As ozone is unstable the reaction is often controlled by ozone decomposition rate rather than the ozonation of dissolved substances (Staehelin and Holgne, 1982).

The pH of water is important because hydroxide ions initiate ozone decomposition involving the following reactions.

$O_3 + OH^* \rightarrow HO_2^{\cdot} + O_2$ $\quad k=70\ M^{-1}s^{-1}$ $\quad$ Eq. 2.11

$O_3 + HO_2^{\cdot} \rightarrow {}^{\cdot}OH + O_2^{\cdot -} + O_2$ $\quad k=2.8 \times 10^6\ M^{-1}s^{-1}$ $\quad$ Eq. 2.12

According to above two equations the initiation of ozone decomposition can be artificially accelerated by increasing the pH or by addition of hydrogen peroxide (Gunten, 2003).

2.6.1 Effect of catalyst on ozonation

From above equations it can be observed that hydrogen peroxide acts as a catalyst in the process accelerating the production of OH^* in ozone decomposition. Conventional ozonation process can be converted to an AOP by:

- Increasing reaction time after addition of ozone
- Increasing the pH
- Adding hydrogen peroxide

The cheapest of the above three options is identified to be addition of hydrogen peroxide (Gunten, 2003). As shown in the equation above, hydrogen peroxide initiates the ozone decomposition by formation of an OH radical and superoxide, which further reacts with ozone according to the following reaction.

$O_3 + O_2^{\cdot -} \rightarrow O_3^{\cdot -} + O_2$ $\quad k=1.6 \times 10^9\ M^{-1}s^{-1}$ $\quad$ Eq. 2.13

The yield of above reaction sequence is one OH radical per decomposed ozone molecule. Main advantage of O_3/H_2O_2 is the acceleration of ozone transformation process.

2.6.2 Effect of ozone on biorefractory COD

Biorefractory COD limits the removal efficiency of biological treatment.
Low ozone doses can ensure sufficient chemical changes in biorefractory compound to enhance wastewater biodegradability (Baig and Liechti, 2001). Therefore, partial ozonation is a good option prior to biological treatment.

Marttinen et al. (2002), used to ozonation to convert slowly biodegradable COD (SBCOD) in leachte to rapidly biodegradable form. An ozone dose of 0.5 mg O_3/ mg COD of municipal leachate, RBCOD value almost doubled, although it was about 20% of the total COD indicating that only a small amount of COD became biodegradable.

2.6.3 Sludge ozonation

Sludge ozonation has been reported to control sludge bulking problems in the conventional activated sludge process (Collington et al., 1994 cited in Ahn et al., 2003). Yasui et al., 1996 cited in Ahn et al. 2002 has studied ozone treatment of excess sludge followed by recirculation into the bioreactor to achieve zero sludge wasting.

2.6.3.1 Sludge settleability

The effectiveness of bioflocculation and settling of activated sludge is characterized by sludge volume index (SVI), defined as the volume in mL occupied by 1 g of sludge after 30 min of settling in 1L cylinder. Lower the SVI better the settleability of sludge. An activated sludge of SVI below 120 is considered satisfactory and over 150 is considered as sludge bulking (Jenkins et al., 1993 cited in Liu and Fang, 2003). In general ozonation tends to increase sludge settleability (Collignon et al., 1994 cited in Ahn et al., undated).

According to Kamiya and Hirotsuji (1998), while observing sludge volume index (SVI) in an intermittent ozonation combined with biological process experiment, the SVI of ozonated slugde was <200 while that of the control reached very high. SVI values towards the end of the experiment indicated good sludge settling characteristics due to ozonation. Also, it has been observed that the relative SVI (ratio of SVI after and before ozonation) reduced with increase of ozone dose on sludge in an intermittent ozonation experiment. In addition to the sludge settling characteristics, experiments have shown that intermittent ozonation combined with biological process has resulted in a cut down of 50% sludge generation with only 30% of the ozone required for continuous operation.

2.6.3.2 Sludge dewaterability

Sludge dewaterability could be examined by capillary suction time test (CST). CST is the time required for the filtrate of sludge to flow by capillary suction pressure outwardly between two concentric circles on a filter paper (Guan et al., 2003). The normalized CST result is obtained by dividing the measured CST by the percentage of solids in the sample.

2.6.3.3 Sludge solubilization & mineralisation

Destruction of cell walls of microorganisms takes place during ozonation of sludge allowing release of cytoplasm into solution (Ahn et al., 2002). Figure 2.5 presents a study on sludge ozonation.

During sludge ozonation, organic matter decomposition occurs in two steps.

1. Solubilization due to disintegration of suspended solids
2. Mineralization due to oxidation of soluble organic matter.

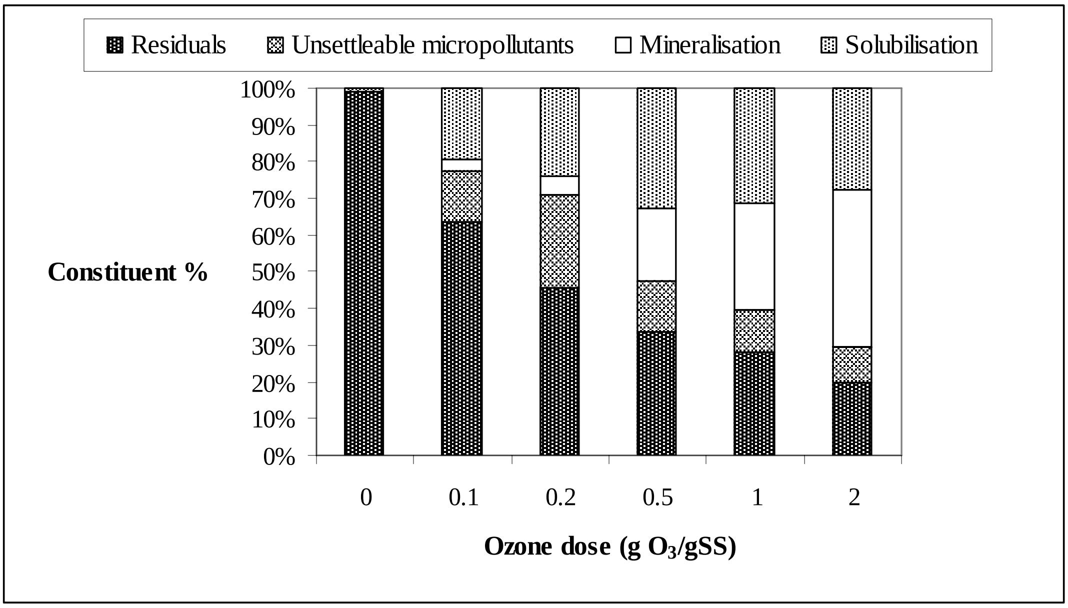


Figure 2.5 Characteristics of ozonated sludge (Ahn et al., 2002)

Mineralization can be defined as difference between the total CODs (TCODs) before and after ozonation. Sludge ozonation asymptotically increases the soluble COD (Ahn et al, 2002).

Mineralization and solubilization are expected to increase during the sludge ozonation due to cell disintegration and hydrolysis, and subsequent oxidation of the solubalized organics into CO_2. Mineralisation also contributes to sludge mass and volume reduction.

2.6.3.4 Sludge biodegradability

Biodegradability can be present as rapid biodegradability and slow biodegradability. Rapidly biodegradable COD (RBCOD) is found by a method based on oxygen uptake rate (OUR) (Xu and Hasselblad, 1996). OUR, shall not be measured until half an hour after ending ozonation to let the dissolved ozone to degrade. The portion of slowly or non biodegradable COD (S/NBCOD) is calculated by subtracting RBCOD from total COD.

2.6.3.5 Toxicity of leachate

Examples of toxic soluble pollutants are chlorinated aromatics, phenols, dyes, pesticides etc. Toxicity can be treated biologically. But toxicity reduction by ozonation is an expensive option.

There are different acute toxicity tests available. One is *Daphnia* acute toxicity test which is modified from ISO, 1996. Another is algal growth inhibition test, modified from SFS-EN28692, 1993 cited in in Marttinen et al., 2002. In each case the toxicity is expressed LC_{50}, which causes death to 50% of *Daphnia* or as EC_{50} that inhibits the growth of algae by 50%.

According to Marttinen et al. (2002), toxicity of leachate could not be effectively removed by air stripping or ozonation.

Leachate toxicity is reported to be correlated to ammonia and COD by Cameron & Koch (1980) & Clement et al. (1997) cited in Marttinen et al., 2002. This suggests that the leachate toxicity will be reduced when COD or ammonia is removed from leachate. Also it is recommended to use several test species for toxicity testing because their different sensitivity to same compound as well as to different toxicants. Sometimes ozonation may increase toxicity.

2.7 Molecular weight cut off

Molecular weight cut off (MWCO) is defined as the molecular weight at which 90% of the solutes are rejected by a membrane (Jimenez et al., 2004).

In electing a membrane size, the selected membrane rating will cut off 0.2 to 0.3 times the value of the molecular weight targeted for retention. For example to retain 50,000 molecular weight, a membrane of rating, 10 -15 kDa shall be used.

Cut off can be affected by factors such as shape and the nature of the targeted species, pH and ionic strength, membrane characteristics, Tangential flow velocity, concentration, membrane life cycle. Particle shape and alignment play important role on cut off, which makes it a statistical process rather than an absolute retention value. Solubility of particles also pays a role in the process, which can lead to precipitation on the membrane surface changing the apparent retention characteristics of the system. pH can change the shape if protein molecules affecting the retention characteristics. Such variation can lead to situations such as 64kD molecule behave as 300 kDa molecule and can be full retained in 100 kDa membrane. This is due to increase of apparent size of a molecule by formation of an ionic cloud around the molecule in a low ionic strength solution. Membrane ratings are nominal as the pores are not absolute in size. As a rule of thumb basis of membrane capacity is to retain approximately 80-90% of a 10,000 molecular weight particles from a “typical” solution. In fact the pores in a membrane are not absolute in size. The pores operate in a statistical basis. Tangential velocity is an important factor determining the gel layer thickness. Low tangential velocity makes the gel layer thicker than high tangential velocity. The mechanism involved is the sweeping away of the concentrated gel forming molecules by the tangential velocity component. This is why the stirred filtration is efficient than non stirred filtration.

3.6 Analytical Methods

Table 3.5 Analytical methods

Parameter	**Method**	**Range**	**Interference** **(Method of elimination)**	**Reference**
Ozone concentration in gas phase (mg/L)	Iodometric method		H_2O_2, organic peroxides, Chlorine	APHA, 1998
Ozone concentration in liquid phase (mg/L)	Spectrophotometric method		Color, turbidity, the presence of organic matter	Shechter,1973
Color (ADMI)	Spectrophotometric method		Turbidity (Filtration of sample)	APHA, 1998
N- Amonia (mg/L)	Colorimetric, Titrometric, Potentiometric- Distillation Procedure	0.05 to 1 mg NH_3-N/1 for colorimetric, 1.0 to 25 mg/l for titrometric and 0.05 to 1400 mg/l for electrode method	Aromatic & aliphatic amines and other organic inorganic compounds will form turbidity upon addition of Nessler reagent. So distillation done. Cyanate hydrolization at pH 9.5. Volatile alkaline compounds-some could be eliminated by boiling at low pH (=2-3) before distillation Residual Chlorine need to be removed by pretreatment of the sample with $Na_2S_2O_4$ before distillation	APHA, 1998
TKN (mg/L)	Colorometric, Titrimetric, Potentiometric	Titrimetric method for concentrations >1mg N/L Nesslerrization method for concentrations <1mg/L Potentiometric metod for concentrations 0.05-1400 mg/L	High NO^-_3 (10X or more than TKN) result in low TKN values. Remove nitrate by ion exchange resin.	APHA, 1998
BOD, 5 day, 20^0 C (mg/L)	Oxi Top Bottles	0-4000 mg/L	Nitrification. Control by the use of a nitrification inhibitor.	

Table 3.5 Analytical Methods (Contd.)

Parameter	**Method**	**Range**	**Interference (Method of elimination)**	**Reference**
COD (mg/L)	Titrimetric method	Mid Level >50mg/L	Organic material from glassware or atmosphere Loss of volatile materials when sample temperature rise during sulfuric acid addition step. Cooling the flask at this stage. Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate to complex the chlorides.	APHA, 1998
TOC (mg/L)	Combustion or Oxidation method	>1mg/L	Carbonate and Bicarbonate carbon.	APHA, 1998
TOC (mg/L)	TOC analyser	>20 mg/L		
pH	pH meter	1-14		APHA, 1998
DO (mg/L)	DO meter			
MLSS (mg/L)	Gravimetric (Glass fiber filter)	Sample dry residue 2.5 – 200 mg	Large floating particles and high dissolved solids content	APHA, 1998
MLVSS (mg/L)	Gravimetric (Glass fiber filter)	Sample dry residue 2.5 – 200 mg	High fixed solids concentration	APHA, 1998

Chapter 3

Methodology

3.1 Introduction

Simulated leachate of COD 7000-9000 mg/L was used for the experiment. Ammonia stripping was carried out first. Thereafter, the leachate was subjected to biological process and physical separation in the membrane bioreactor. Subsequently advanced oxidation of MBR effluent with ozone and recirculation of effluent were carried out in order to achieve improved effluent quality. .

Landfill leachate required for this experiment was obtained from Pathumthani Sanitary Landfill (Pathumthani province, Thailand) and Ramindra Transfer Station (Bangkok, Thailand). These leachates were mixed in suitable proportion to simulate a medium-age leachate with COD range of 7,000-9,000 mg/L and NH_3 N 1,800 - 2,000 mg/L.

3.2 Overall experimental plan

Present study investigates on the efficiency of treatability of ammonia stripped leachate using membrane bioreactor coupled ozonation process. First the ammonia stripping process is established. Then the efficiency of MBR is investigated. Subsequently the effect of ozonation on MBR effluent and effluent recirculation is studied. Ozonation is carried out for treating MBR effluent at the optimum ozone concentration established under a previous study. Overall experimental plan is shown in the figure 3.1.

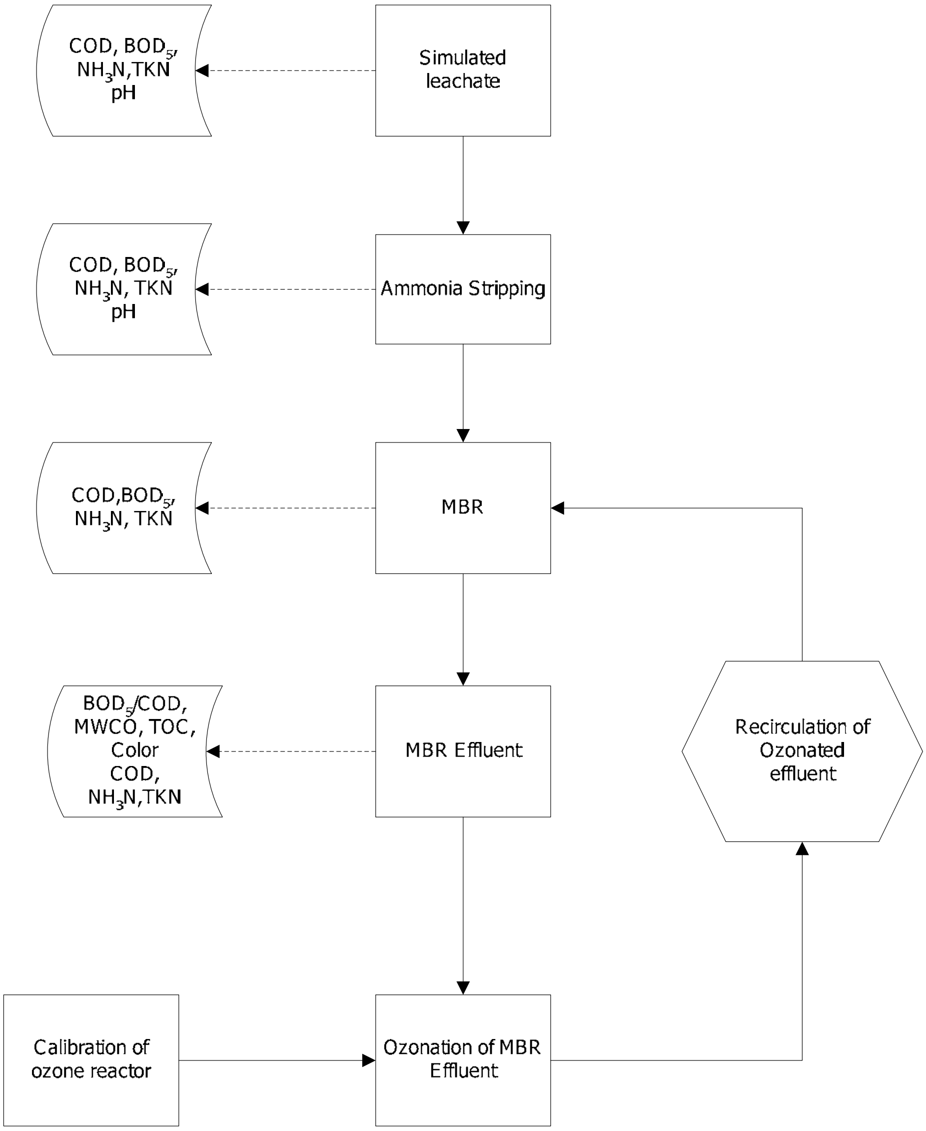


Figure 3.1 Overall experimental plan

3.3 Experimental set-up

Experimental setup mainly consists of three processes, ammonia stripping, membrane bioreactor and ozonation process. Each process has related experimental apparatus as described below.

3.3.1 Ammonia stripping unit

The method used for ammonia stripping under this study has been selected out of two available methods for ammonia stripping, namely pH driven and thermal driven. For thermal driven process the energy could be obtained from the leachate gases. A temperature of 65-70 ^{0}C can give better performance in ammonia removal. In the pH driven method used in this study, the pH of the mixed leachate is increased to between 11 and 12 by adding lime or NaOH. Adding NaOH is selected to minimize the sludge production when compared with adding $Ca(OH)_2$. In this experiment, a mechanical stirring arrangement in a tank is adopted. Ammonia stripping is an economic means of removing nitrogen rather than removing the same via nitrification and denitrification process in a biological reactor.

This pH driven physico chemical method for ammonia stripping, mainly consisting of pH elevation and mechanical stirring has been established under a previous study by Wichitsathian (2004). In this study the results are verified with the previous test results.

Ammonia stripping unit consists of a cylindrical tank with mechanical stirrer arrangement of capacity about 90L. About 30L of mixed leachate is stripped in the tank at a time. Stripping is done by mechanically stirring the mixed leachate after raising the pH to between 11 –12 from around 7.5 in mixed leachate. After stripping the leachate is transferred into a settling column of capacity about 10L. Stripped leachate is allowed to settle for about 3h. Then the scum and settled portions removed. After settling the pH is reduced to around 8 before feeding to the MBR.

Ammonia striping test was conducted according to the method described above for 2h., 4h. and 5h.. stripping times to verify the best stripping time with respect to the NH_3-N removal efficiency. COD, BOD_5 and TKN are also tested to observe the efficiency of the method. Process is outlined in figure 3.2.

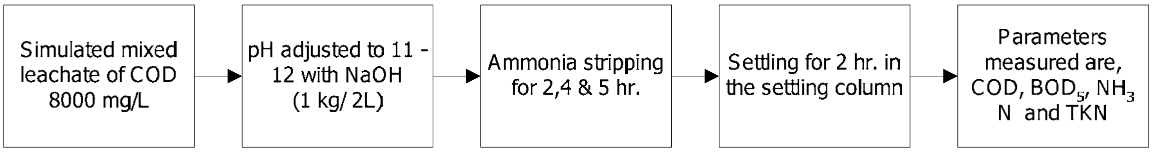


Figure 3.2 Ammonia stripping process

3.3.2 Membrane bioreactor (MBR)

3.3.2.1 Membrane bioreactor design

The MBR is designed to suit the operational conditions given in section 3.2.2.2. Membrane properties are as give in the Table 3.1. The internal diameter of the reactor is selected as 12 cm**.** Suction, air backwash and air release operations are automated by a timer and associated solenoid valves. Details of the reactor are given in Figure 3.3.

MBR consists of inlet level control tank, membrane bio-reactor and a suction pump. pH in the reactor is controlled to be between 7.0 to 7.5 by adding 10% commercial grade sulfuric acid by automatic chemical feeding pump controlled by a pH controller fitted with a pH probe. Dissolved oxygen (DO) is controlled to create aerobic conditions in the reactor by adjusting the air flow rate upon manual DO measurement to maintain a concentration above 2 mg/L. An air flow of 2-3 L/min at 6 bar pressure is used for this purpose. A peristaltic pump is used for suction of permeate from the hollow fiber membrane. MBR is operated in a 29 minutes cycle consisting of 25 minutes of suction, 3 minutes of air backwash at 1 bar pressure and one minute of air release. Operating reactor volume is 6L. Simulated leachate is treated in membrane bioreactor under mixed bacteria culture.

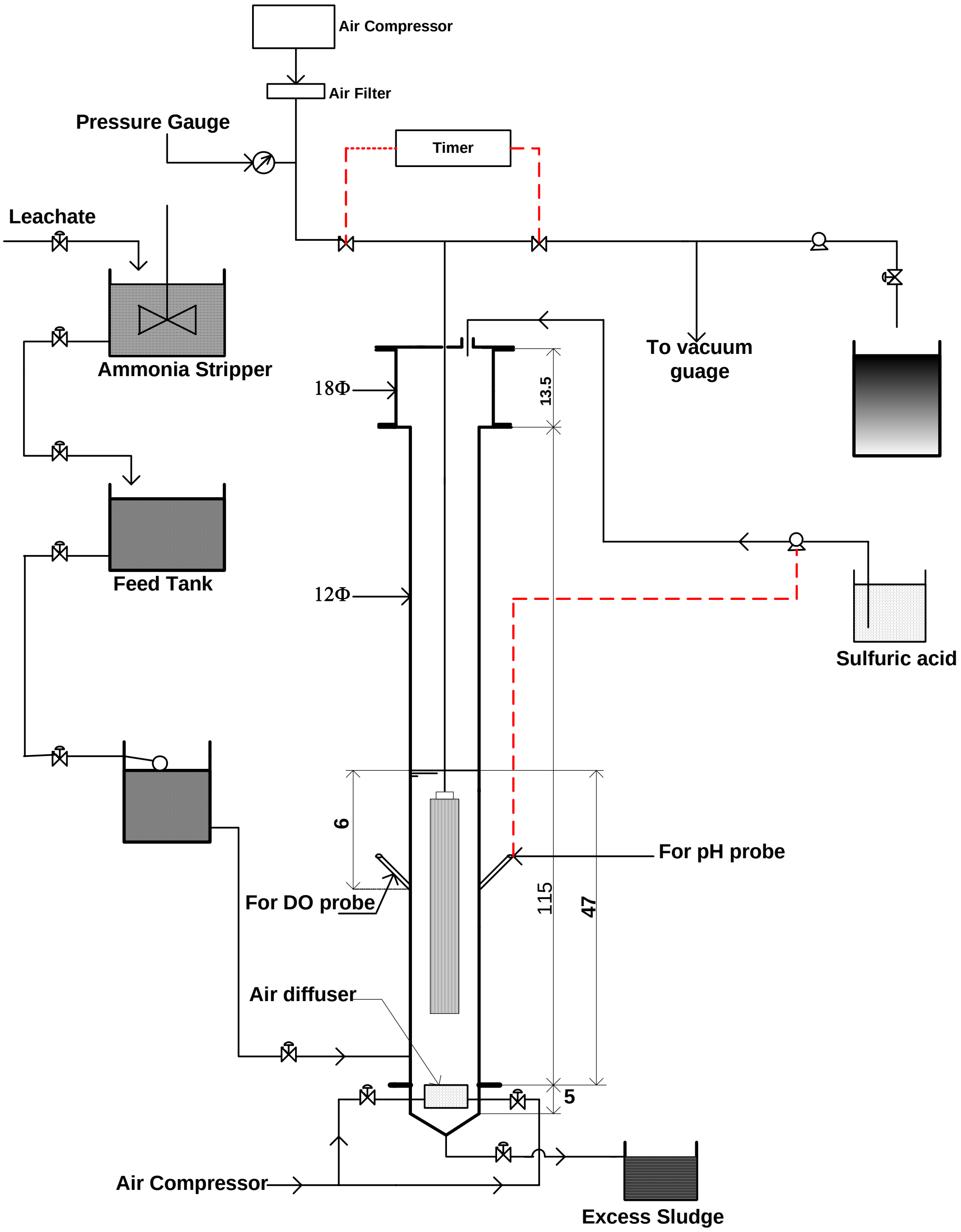
3.3.2.2 MBR operating conditions

Table 3.1 MBR properties

Reactor Volume	6 L
HRT	24 h
MLSS	10,000-12,000 mg/L
Membrane material	Polyethylene
Membrane type	Hollow fiber
Pore size	0.1 μm
Surface area	0.42 m^2

Table 3.2 MBR operating conditions

Parameters	**Operating Conditions**
HRT	24 h
Flow rate	120 ± 10 mL/cycle
MLSS	10,000 mg/L
MLVSS	7,000 mg/L
DO	2-4 mg/L
pH	6.8-7.5
Temperature	28-30^{o}C
Transmembrane pressure	< 80 kPa



(All dimensions are in centimeters)

Figure 3.3 MBR operation drawing

MBR operating conditions are shown in the Table 3.2. The HRT has been established to be 24 hr. in a previous study by Wichitsathian (2004). Also according to a similar study by Yoon et al. (2004), the HRT shall be close to 24 hr. to have the desired 10,000 mg/L MLSS range.

Optimum operating conditions of the membrane bioreactor is studied by monitoring COD, MLSS, MLVSS, TKN, NH_3-N and pH. Steady operation of MBR is achieved with respect to HRT. SRT was calculated based on the maintained MLSS value which is 10,000 - 12,000 mg/L. Overall operational parameter testing plan was as shown in Table 3.3.

Table 3.3 MBR operating parameters

Sample location	**Parameter**	**Frequency of testing**
Mixed raw leachate	COD, NH_4^+N, pH	Weekly
Ammonia stripped and settled leachate	COD, BOD_5, NH_4^+N, TKN	Weekly
MBR mixed liquor	pH, DO, TMP, Flux MLSS , MLVSS	Daily Once in two days
MBR effluent	COD, BOD_5, NH_4^+N, TKN	Weekly

3.3.2.3 Foaming in MBR

Foaming is one of the main problems observed in the membrane bioreactor. To address this problem, the previous design of the reactor was modified by incorporating an enlarged cylindrical section at the top of the reactor. Also two perforated plates were introduced, one at the top of the reactor and the other just above the membrane module as means of mechanical foam breakers. In addition to these measures, an automatic antifoam feeder has been installed. This was a simple device with a gravity feed tank containing antifoam solution of dilution 1:200 fitted with a timer controlled normally closed solenoid valve.

Mechanical means of foam breaking was preferred to chemical means as antifoam contributes to the increase of COD in MBR thus affecting the expected results.

3.3.2.4 Activated sludge acclimatization

Acclimatization of activated sludge was done as a batch process in a separate container of about 10 liter volume. Procedure consisted aeration for 21 hrs. and settling for 3 hrs. pH was maintained 7.0 – 7.5 by addition of sulfuric acid or Sodium hydroxide. At the end of 3 hr settling period, 2 L of supernatant is replaced with mixed leachate of medium age.

3.3.2.5 Membrane cleaning

Membrane fouling creates the need for membrane cleaning. Air back flushing and chemical cleaning were the methods applied for cleaning the membrane. Air backflush was built into the membrane cycle, which was performed for 3 minutes at 1 bar pressure. Membrane was chemically cleaned when the trans-membrane pressure reached about 80 kPa. Chemical cleaning was carried out as per the procedure recommended by the manufacturer, Mitsubishi Rayon. Mixed solution of sodium hyphochlorite (effective concentration 3,000 mg/L) and 4% (weight/volume) aqueous sodium hydroxide was used. Cleaning was done by immersing the membrane in the mixed solution for 6 to 24 hrs. Subsequently the membrane was immersed and rinsed in DI water. Finally the membrane resistance was measured.

Membrane resistance was calculated using the equation 2.5 by suction pumping of DI water through the membrane using a peristaltic pump. Flux was gradually increased to receive set of readings for transmembrane pressure. Membrane resistance was obtained from a plot of transmembrane pressure vs. flux.

3.3.2.6 Maintaining activated sludge properties

Following techniques were adopted to minimize difficulties experienced in maintaining activated sludge properties in the reactor.

1. Reduction of sludge age by recirculating with externally acclimatized sludge.
2. Feeding protein and glucose to improve MLSS. A dose of 2.82 g glucose and 3 g soya protein mixed into 12 L of feed to MBR in alternative days was used until improvement of MLSS.
3. When MLSS was in excess of 12,000 mg/L, excess sludge was withdrawn to maintain the MLSS within 10,000 mg/L range.

Effluent quality and membrane fouling were considered as parameters to observe MBR efficiency.

3.3.2.7 MBR efficiency

Treatment efficiency of the MBR was measured mainly with respect to COD removal. Removal efficiencies of BOD_5, NH_3-N and TKN were also monitored.

3.3.2.8 Sludge characteristics

Sludge characteristics were measured in terms of MLSS, MLVSS, CST, DSVI, EPS and viscosity. Methodologies which are not covered in APHA(1998) are detailed below.

a. EPS analysis

There is no standardized method for EPS extraction. Therefore difficulties arise in interpreting results from different methods (Liu and Fang, 2003). In this experiment Lowry’s method is used for Protein analysis and Phenolic sulfuric acid method is used for Carbohydrate analysis. The procedure is outlined in the figure 3.4.

Chemical reagents used for EPS analysis are as following:

Solution A, 100 mL: 0.5 g$CuSO_4.5H_2O$
1 g $Na_3C_6H_5O_7(2H_2O)$ (Sodium citrate)

Solution B, 1L: 20g Na_2CO_3
4 g NaOH

Solution C, 51 mL; 1 mL solution A
50 mL solution B

Solution D, 20mL; 10 mL Folin-Ciocalteu phenol reagent

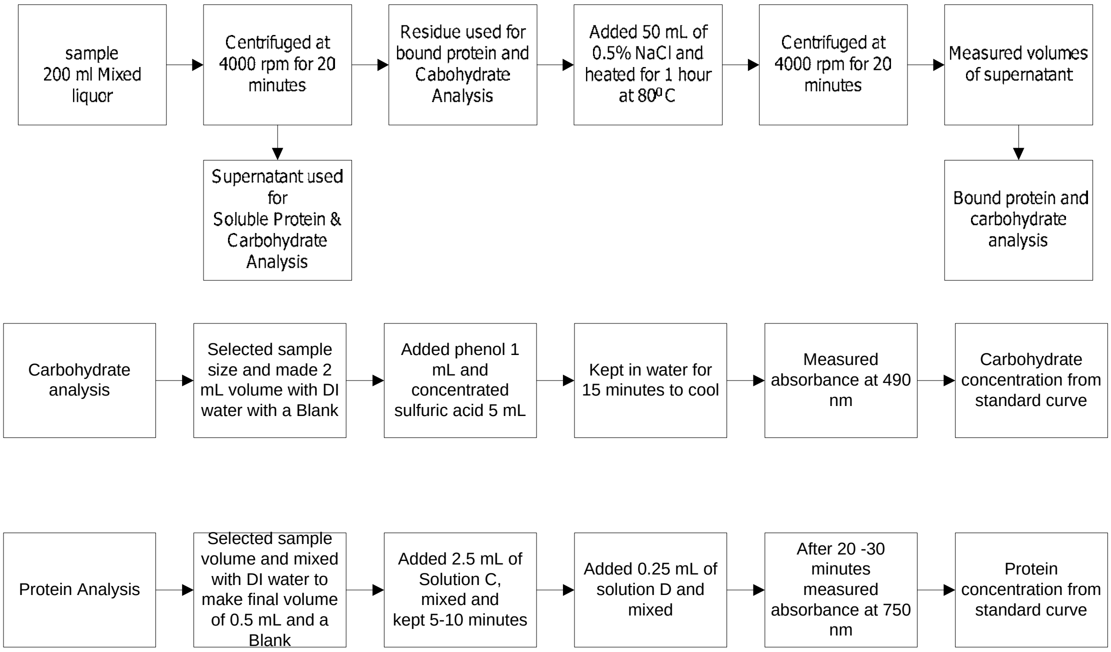


Figure 3.4 Methodology for protein and carbohydrate analysis

b. Diluted sludge volume index (DSVI)

DSVI is calculated using the equation 2.4. As SVI gives poor description of settleablility as the results strongly depend on the concentration of MLSS, Anderson and Sigvardsen (1996) suggest to use DSVI with MLSS diluted to 1-2 kg SS/ m^3. As MLSS concentration was very high in this experiment DSVI was used to analyze settleability.

c. Viscosity

Viscosity was measured using a viscometer. Conditions under which the measurement was taken such as spindle rotation speed, torque and temperature were recorded.

3.3.3 Ozonation phase

After achieving steady state of treatment in the MBR, the effluent was ozonated. The main components of the instruments used in the ozonation phase were ozone generator, ozone column reactor and ozone scraper.

3.3.3.1 Ozone generator

Pure oxygen was used to generate ozone by corona discharge method as shown in figure 3.5. Dry oxygen is passed between two electrically charged plates separated by a ceramic dielectric medium and narrow discharge gap. Part of the oxygen is converted to ozone.

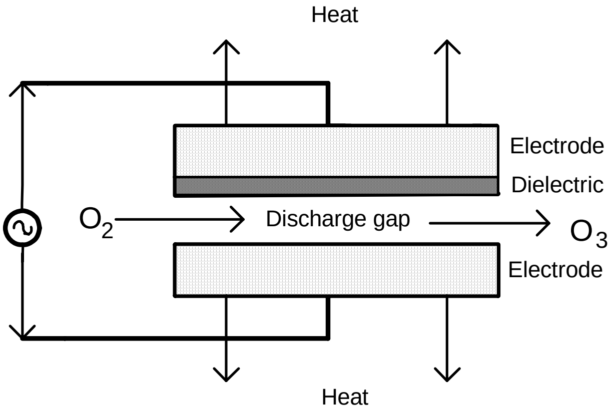


Figure 3.5 Corona discharge method

3.3.3.2 Ozone column reactor

The ozone column reactor is an ideal plug flow reactor, where ozone can continuously introduced into the solution. Gaseous ozone was continuously fed into the reactor in both batch and continuous operation modes. Upper portion of the reactor is a glass column tube of 40 mm diameter and 160 cm. length. The bottom part of the reactor is fixed with ceramic a diffuser. Detail of the ozone column reactor is shown in figure 3.6.

The piping of the ozonation system consists,

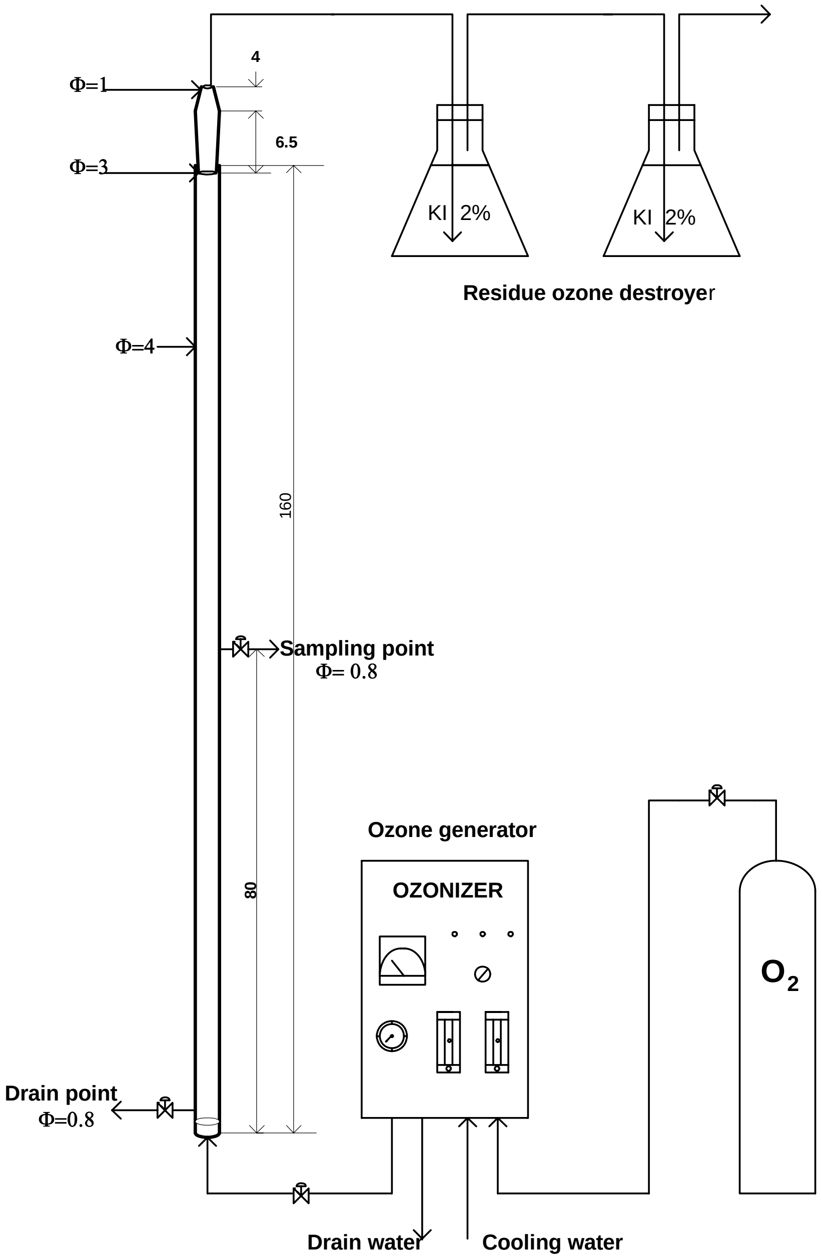
1) Air pipe connecting the air outlet of the rotary air compressor and the air inlet of the ozone generator is made out of PVC.

2) Ozone pipe made out of Teflon is connecting the ozone outlet and the reactor inlet. The reactor end consists of a ceramic diffuser.

Tap water is used for the cooling system.

3.3.3.3 Ozone Scraper

This is the device for trapping excess ozone. The excess ozone gas is transferred from the top of the ozone reactor to two bottles in series containing 2 % potassium iodide (KI) neutral solution. KI directly reacts with ozone in the off gas to prevent any ozone from being emitted to the atmosphere.



(All dimensions are in centimeters)

Figure 3.6 Ozone column reactor

3.4 Operation of ozonation process

Due to practical limitations, online ozonation of MBR effluent cannot be done. Therefore batch study had to be carried out to for leachate ozonation and recirculation experiment.

3.4.1 Ozonation process

3.4.1.1 Calibration of ozone reactor

Ozone reactor was calibrated to find out the characteristics of ozone generated. This was performed for the gas phase and the liquid phase by measuring the ozone concentration in each phase.

Ozone in the gas phase was determined by Iodometric method (APHA, 1998) by using 2% potassium iodide solution to determine the amount of residual ozone in the gas phase. The amount of ozone produced is transferred to react with KI directly. The iodide liberated was treated with 0.3 molar sodium thiosulphate solution.

Reaction of ozone with potassium iodide is given by the following equation.

$$O_3 + 2\,I^- + H_2O \rightarrow I_2 + 2\,OH^- \qquad \text{Eq. 3.1}$$

The released iodine was titrated with sodium thiosulphate according to the following equation.

$$I_2 + 2\,S_2O_3^{\,2-} \Leftrightarrow 2\,I^- + S_4\,O_6^{\,2-} \qquad \text{Eq. 3.2}$$

a) Ozone in gas phase

Ozone demand is given by the following equation.

$$\text{Ozone demand (mg/min.)},\ OD = \frac{A \times N \times 24}{T} \qquad \text{Eq. 3.3}$$

Where A= mL of sodium thiosulphate titrant used
N= normality of sodium thiosulphate solution
T = ozonation contact time

Ozone concentration was calculated as follows;

$$\text{Ozone concentration, mg/L} = \frac{OD \times 60}{AF} \qquad \text{Eq. 3.4}$$

Where AF = Oxygen flow rate (L/h)

b) Ozone in liquid phase

Ozone in the liquid phase is determined by spectrophotometric method. The method involved oxidation of a buffered iodide solution and spectrophotometric measurement of the triiodine ion liberated by ozone. (Stretcher, 1973)

Calibration curve was prepared using 0.0001 N iodine solution assuming ozone is simulated by iodine. 0.01 N iodine solution was diluted 100 times to receive a solution equivalent to contain 0.0024 mg of ozone in 1 mL iodine solution. This iodine solution was used to simulate different ozone concentrations to draw a calibration curve of absorbance vs. ozone concentration using spectrophotometer as detailed by Stretcher, 1973. 10 mL sample was prepared by adding neutral KI solution to the required iodine solution volume and absorbance was measured by spectrophotometer. The calibration curve absorbance vs. ozone concentration could be used to find the ozone concentration in liquid phase.

$$\text{Ozone Transfer Efficiency (\%)} = \frac{O_{3\ \text{aqueous}}}{O_{3\ \text{feed}}} \times 100 \qquad \text{Eq. 3.5}$$

Ozone mass transfer from gas to liquid phase can be found by following equation.

$$\ln (C_L^* - C_L) = - K_L a \times t \qquad \text{Eq. 3.6}$$

C_L^* and C_L are the equilibrium ozone concentration in mg/L and ozone concentration in aqueous phase (mg/L) at time t respectively. K_La is the ozone mass transfer coefficient ($time^{-1}$) and t is contact time.

3.4.1.2. Optimization of ozonation process by batch study

A Batch study was conducted to understand the variation of MBR effluent properties in terms of COD, BOD_5 and color due to ozonation. Ozonation was varied by using different contact times, 15, 30, 45 and 60 minutes for the same ozone concentration of 75 mg/L. This ozone concentration has been optimized by a previous study by Chaturapruek (2003).

BOD_5: COD ratio is the ideal ratio for parameter optimization in MBR /ozonation system. However due to longer time required for BOD_5 determination, COD was used as the indicator parameter. In addition to this, TOC and color were used as parameters.

3.5 Molecular weight cut off study

Molecular weight distribution of leachate constitutes gives an idea of the efficiency of leachate in biodgradation and an indication about the refractory nature of the molecules. Therefore a molecular weight cut off study as described below was carried out. Process apparatus are shown in figure 3.7. The procedure is described in figure 3.8.

a) Determination of initial membrane resistance

Membrane resistance test was conducted to find out the efficiency of the new membrane. It is measured by filtrating distilled water through the membrane using Nitrogen gas up to 5 bar pressure in one bar increments. The volume of the permeate from membrane is measured using an electronic balance taking density of water equal to 1 kg/L. Membranes of four different molecular weight cut off sizes, namely 100 kDa, 50 kDa, 10 kDa, and 5 kDa were used in the experiment. The diameter of each membrane was 4.7 cm., where the effective filtration diameter was 4.2 cm. Membrane resistance was calculated using the formula given below.

$$\mathbf{J = \frac{TMP}{\mu R_m}} \qquad \text{Eq. 3.7}$$

J = Filtration flux (L/m^2.h)
TMP = Transmembrane pressure (kPa)
μ = Dynamic viscosity = 0.798*10^{-3} N.s/m^2 at 27 ^{o}C
R_m = Membrane Resistance (m^{-1})

b) Molecular Weight Cut-Off (MWCO) experiment

Molecular Weight Cut-Off experiment separates the organic molecules of the leachate on the basis of their molecular weight. Flat sheet circular ultra filtration (UF) membrane of 4.7 cm diameter was used. Molecular weight cut-off ranges and the description of four types of ultra filtration membranes used in the experiment are shown in table 3.4. Commercial grade Nitrogen gas was used to pressurize the ultrafiltration cells. The MWCO cutoff out put was categorized into groups; 1) MW >100 kDa, 2) MW 50-100 kDa, 3) MW 10-50 kDa, 4) MW 5-10 kDa, 5) MW < 5kDa.

MWCO was performed on MBR influent, MBR effluent and the ozonated MBR effluent. Stirred and non stirred tests were carried under the MWCO test. Non stirred test was performed on a “Sartorius” brand stainless steel module SM 16249 capable of operating at a working pressure of 10 bars. Stirred test was performed on a plastic module “Sartorius” brand plastic module SM 16526 capable of working upto 7 bar pressure. For safety reasons membrane resistance measurement tests which needed up to 5 bar peressurization were performed in the stainless steel module for all cases.

c) Standardization of MWCO experiment

Preliminary tests indicated that the leachate did not show proper filtration due to it filter clogging properties. Therefore the experimental procedure needed to be standardized. Standardization was done on stirred and non stirred modules with varying leachate dilutions with DI water.

The stanadradized procedure for MWCO experiment is as given below:

1. Sample was filtered through 0.45 μm filter paper in order to remove suspended solid from the sample.

2. Leachate sample was diluted 1:1 with DI water

3. 200 mL of diluted sample was used on 100 kDa UF paper in stirred MWCO module. Stirred test was performed with Nitrogen gas at 2 bars for 30 minutes.

4. The volume of retentate representing the fraction of MW > 100 kDa was preserved for analysis.

5. The volume of permeate was used as an initial volume for UF at MW 50 kDa.

6. The same procedure was repeated with UF membrane sizes 10 and 5 kDa.

7. Outcome of each MW fraction was analyzed for COD and TOC.

8. COD and TOC mass balance of MWCO fractionation was carried-out.

Table 3.4 Range of MWCO membranes used in the experiment and their specifications

MWCO (kDa)	**Specification**
100	Koch membrane M-180, 0030887 series
50	Koch membrane M-100, 0030883 series
10	Koch membrane K-131, 0030880 series
5	Koch membrane K-328, 0030896 series

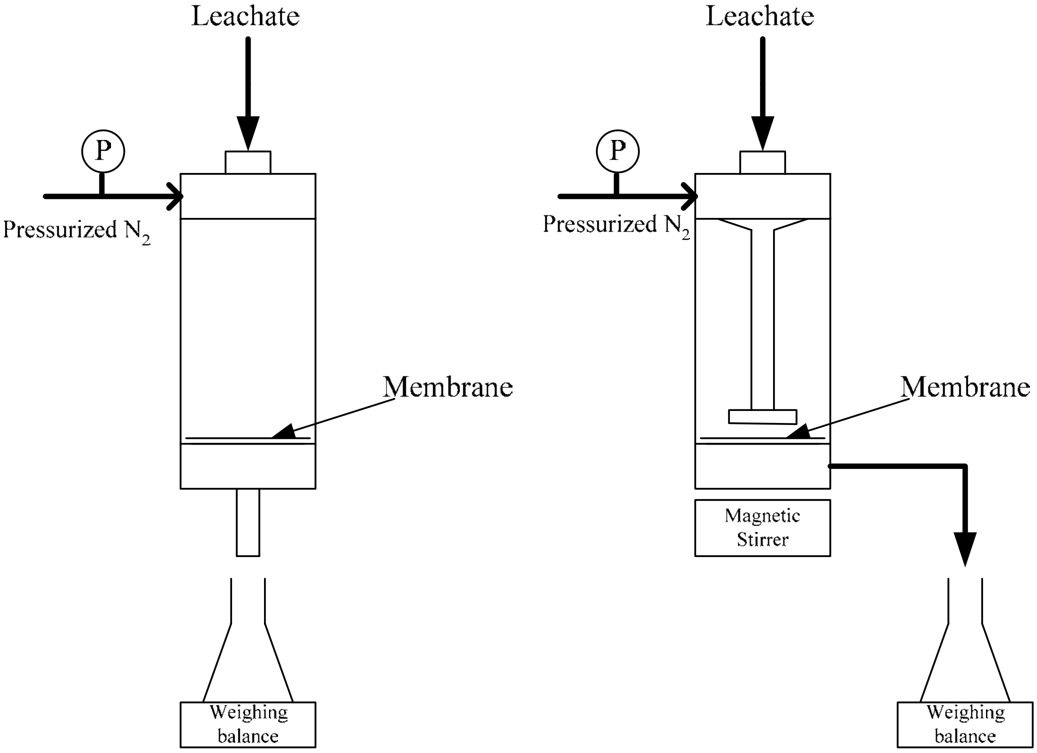


Figure 3.7 Ultrafiltration process for MWCO experiment non stirred and stirred test

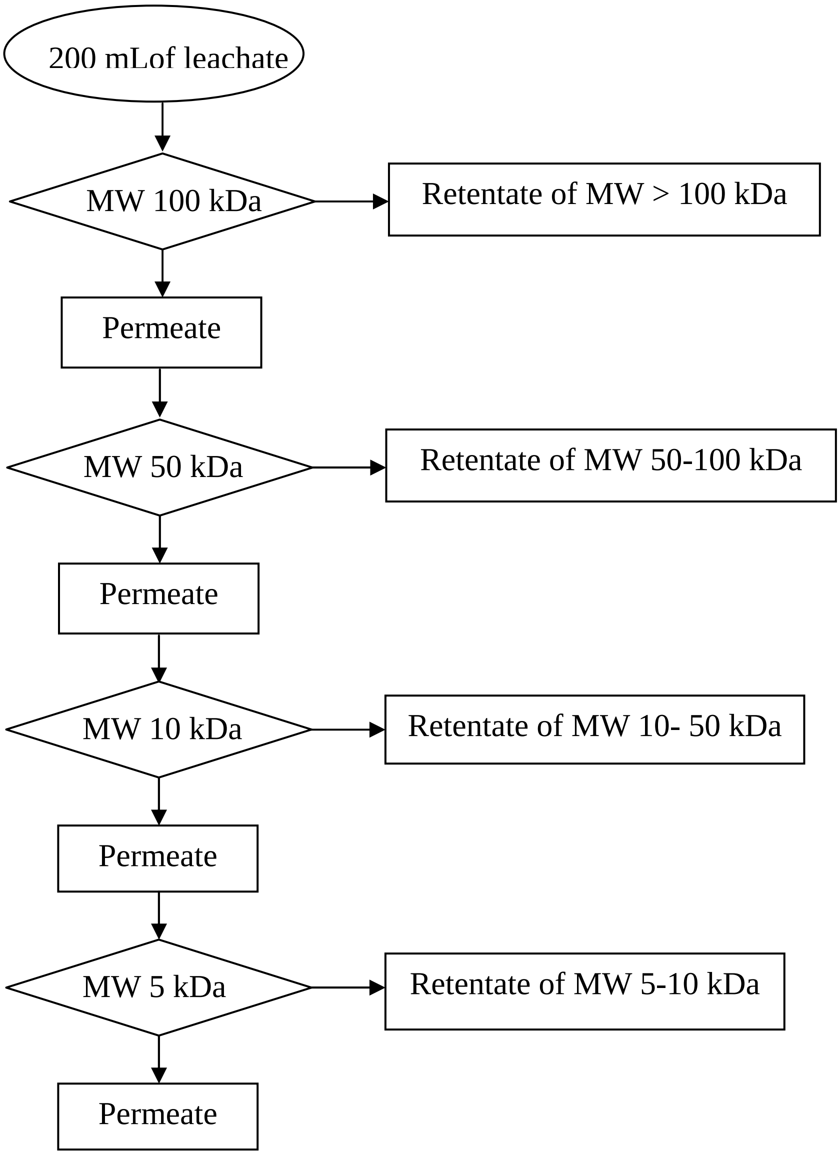


Figure 3.8 Procedure for Molecular Weight Cut-Off experiment

Chapter 4

Results and Discussion

4.1 Mixing leachate

Young leachate has high BOD_5 in the range of 60,000 mg/L and low ammonia nitrogen in the range of 300 to 500mg/L and old leachate has low BOD in the range of 1000 to 2000 mg/L and high ammonia nitrogen in the range of 1000 to 2000 mg/L . BOD reduction and ammonia N increase in leachates occur due to natural biological process occurring in a landfill.

The maximum F/M ratio for successful operation of biological process is 1.5 kg BOD_5/kg MLSS.d. As explained in 3.3.2.2 the optimum operating MLSS for MBR is about 10,000 mg/L. The limiting BOD_5 loading for operation should be 15,000 mg/L. Generally the BOD_5 of young leachate vary from 20,000 to 60,000 mg/L making biological process inefficient for treatment of such leachate. On the other hand the minimum F/M ratio for biological process is around 0.05 kgBOD_5/ kg MLSS.d, which means about 500 mg/L BOD_5 for MBR influent. Also the high ammonia content in old leachate inhibits the biological process. Therefore medium age leachate is the ideal for optimum operation of MBR biological process. Therefore young leachate from Ramindra transfer station and old leachate from Pathumthani site are mixed together to achieve medium aged leachate required for the experiment. Properties of the raw leachate used are given in Table 4.1 below and are detailed in Table B.1 of Appendix B.

Table 4.1 Properties of raw leachate

	pH	**COD (mg/L)**	**BOD (mg/L)**	**NH_4^+-N (mg/L)**
Ram-Indra leachate	3.8	69,667	60,700	448
Pathumthani leachate	8.2	3,542	1,350	1,120

4.2 Ammonia Stripping

In old leachates the ammonia level generally exceeds 1000 mg/L. Biological process is not efficient in removal of such high ammonia levels. Toxicity of high ammonia content inhibits the biological process. Also aerobic biological process converts ammonia to nitrates which can cause eutrophication problems when released to the environment.

The first stage of waste degradation is a brief aerobic phase using the available oxygen which is followed by anaerobic degradation in two stages. In the first stage, acetogenic degradation involves partial breakdown of organic materials producing high concentrations of organic acids and corresponding high BOD and COD. In the second stage known as methanogenic degradation, partially degraded organics are converted to methane and carbon dioxide. COD and BOD fall correspondingly. Ammonia in old leachate is thus produced by breakdown of proteins to amino acids which are then deaminated, releasing the ammonia as the ammonium ion. Anaerobic conditions are predominant in the landfill body, which are unfavourable for conversion of ammonium. Therefore ammonia accumulates.

As removal of ammonia in leachate under physico chemical pretreatment is economical, an experiment was conducted to find out the stripping efficiency variation with the stripping time.

Table 4.2 Ammonia stripping test results

Stripping time (h)	**COD (mg/L)**	**NH_4^+ N**	**BOD_5**	**pH**	**$\frac{BOD_5}{COD}$**
0	8,065	1,022	3,388	12.00	0.42
2	7,279	784	2,766	11.13	0.38
4	6,984	560	2,653	10.95	0.38
5	6,784	490	2,540	10.94	0.37

According to Table 4.2, the 5hr. ammonia removal efficiency is 52%. Average ammonia stripping efficiency of about 59 ± 14% could be achieved through the method adopted in this experiment according to the details given in Tables B2, B3 and B5 of Appendix B. In the work of Wichitsathian (2004), the BOD_5 of the simulated leachate varied between 3,200 to 3,500 mg/L with BOD_5/COD ratio of 0.44-0.45. The above results are comparable with his study according to the results of Table 4.2 above and Table B4 of the Appendix 4. During the work of Wichitsathian (2004), five hour ammonia stripping efficiency was in the range of 80-90%. The ammonia concentration of present mixed leachate is in the range of 1000-2000 mg/L. This is a wider range than that of Whichitsathian (2004) which was in the range of 1300 to 1,800 mg/L. Higher concentration of ammonia in present leachate may be the reason for the reduction in percentage removal efficiency.

Figures 4.1 and 4.2 show the removal efficiencies and variations of NH_3N, COD and BOD_5 with the stripping time. It is observed that the change of stripping efficiency reduces with time and reaches towards a constant for a stripping time of five hours.

According to Thiel (2002) ammonia concentration less than 100 mg/L has no effect on the activated sludge process. But concentrations above 480 mg/L will upset the activated sludge process. Therefore 59% stripping efficiency achieved under the present study could affect the activated sludge process in the MBR. However later in the experiment it was found that activated sludge process operating well with excess sludge production without adding any external nutrients. This confirms acclimatization of microbes to the toxic environment to perform well in contrast to the figures by Thiel (2002) above which have been developed for conventional activated sludge process.

BOD_5 and COD removal also is observed during the ammonia stripping process. This makes BOD_5/COD ratio lower as shown in the figure 4.3 thus making the leachate less bio degradable. Also it is observed that BOD_5/COD ratio converged towards a constant value in the range of 0.37-0.38 with respect to stripping time.

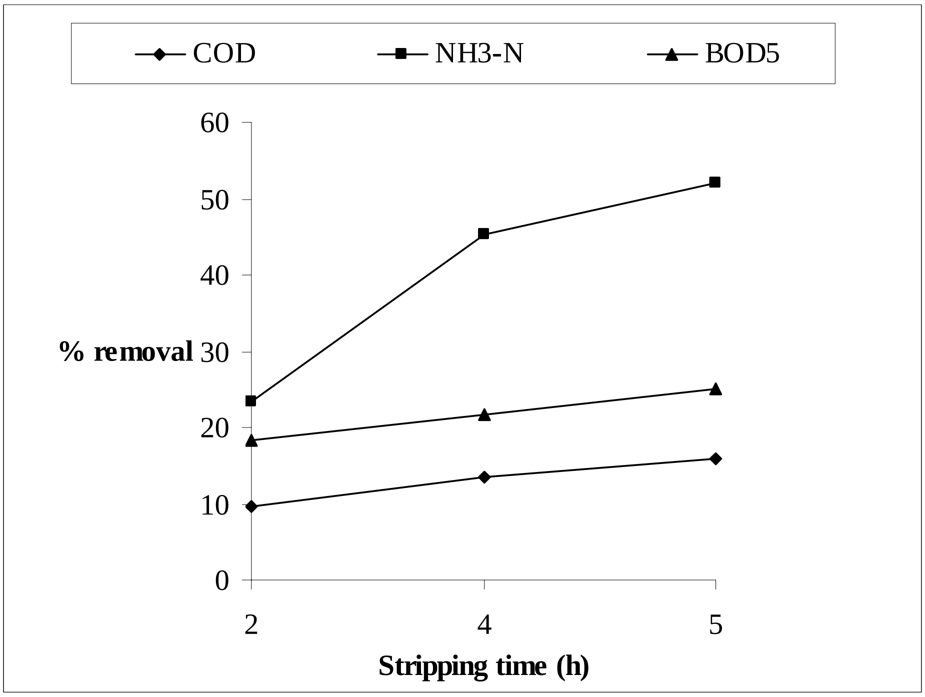


Figure 4.1 Removal efficiencies in ammonia stripping

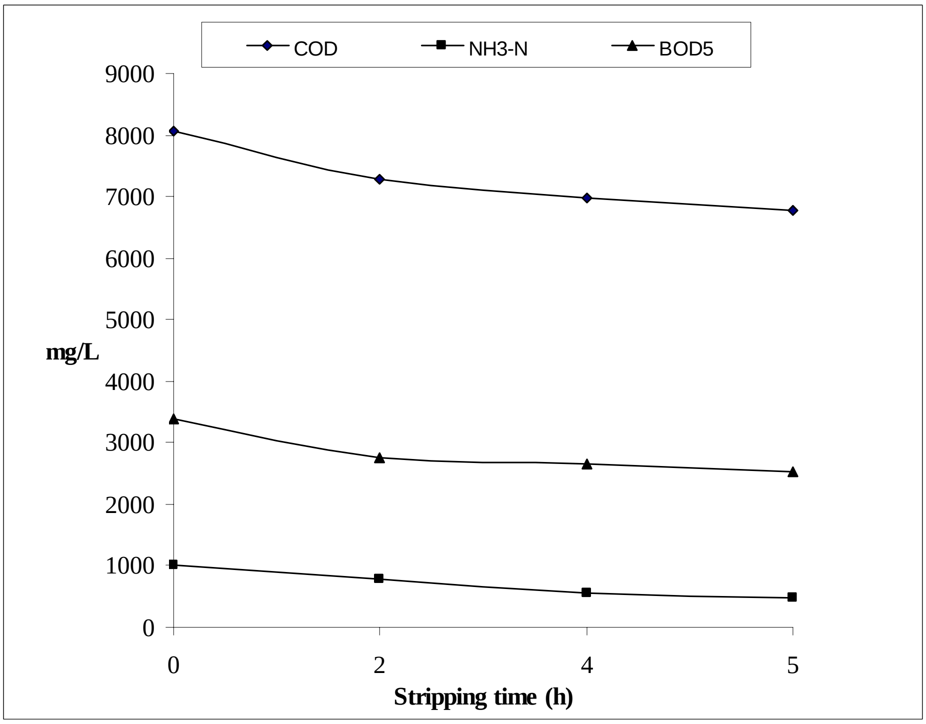


Figure 4.2 Variation of COD, NH_3N and BOD_5 with stripping time

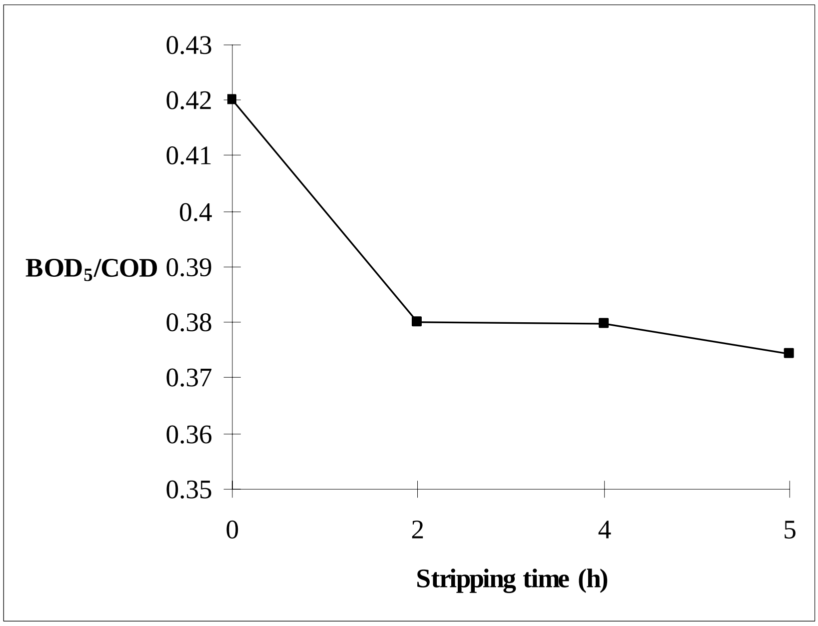


Figure 4.3 Variation of BOD_5/COD with stripping time

BOD_{20} value was measured along with BOD_5 value for comparison. The results are shown in Table B12 of Appendix B. According to the results Table B13 shows the variation of BOD_5/BOD_{20} from 0.72 to 0.76.

4.3 Membrane bioreactor (MBR)

4.3.1 Activated sludge process operational problems

Difficulties were encountered stabilizing the activated sludge process in the MBR. The problem was inability to increase MLSS above 8000 mg/L. High rate of sludge loss was observed reducing MLSS to the range of 1,500 mg/L. along with worm growth inside the reactor. Reasons for the problems encountered could be arttributed to several factors as discussed below.

In the present MBR experiment, the sludge loading rate varied from 0.3 to 1 kg BOD/kg MLSS.d. According to Ekelboom (2000) low F/M ratio <0.025 kg BOD/kg MLSS.d leads to floc disintegration. Therefore low F/M ratio can be rules out from the reason for sludge disintegration observed in the MBR.

In an ideal sludge, filamentous organisms and floc forming organisms grow in balance. The filamentous organisms grow largely inside the flocs, providing a structure and strength to the floc. Such ideal floc will have SVI of 80 to 120 mL/g. In a pin point floc there are few or no filamentous organisms present. Also turbid supernatant is a characteristic of pin point flocs. Such flocs can easily break due to turbulence caused by aeration. Large flocs settle well, but small flocs do not settle well. Such non settling sludge has SVI less than 70 mL/g. (Jenkins et al, 1993). Due to the stabilization problem in the MBR, SVI remained around36 mL/g and contained small particles which did not settle well indicating status as pin point flocs. This was confirmed by the microscopic investigation which showed very few filamentous bacteria, low protozoa and small flocs.

At MLSS 6,300 mg/L, microscopic investigations revealed that there were few discrete flocs with no filamentous bacteria. At MLSS 8,500 mg/L few protozoa and filamentous bacteria were observed with increased sludge particles. At MLSS concentration 23,200 mg/L, number of ciliate type protozoans observed among a dense population of sludge particles.

Toxicity can affect protozoa, the higher form of microbes in activated sludge first. It causes blooming of small free swimming ciliates (kind of protozoa). This is an indication of activated sludge breakup and the production of large number of dispersed bacteria (turbidity), which are food source for free swimming ciliates. Death of protozoa causes white foams containing protozoa and protozoan fragments due to cell lysis and release of cell contents (Ekelboom, 2000). Therefore high level of foaming in MBR could be caused by toxicity, which leads to cell death.

According to Ekelboom (2000), worms being the largest organisms observed in activated sludge consume whole sludge flocs and floc fragments. Therefore worms can be the main reason for sludge reduction observed in the reactor. Worms stand on the top level of the food pyramid (Gray, 1989). Sludge age plays an important role in substrate removal and bacterial growth. Older sludge makes substrate removal slow as they contain more dead cells inside the flocs. Low sludge age helps to reduce higher forms of organisms in the activated sludge while removing substrate efficiently. Therefore sludge wasting was tried as a means of controlling worm growth problem in the reactor.

Due to some of the reasons mentioned above, there was a problem of management of the MBR at steady state with respect to MLSS. MLSS in the MBR varied between 2,000 and 5,000 mg/L during the early stages of the experiment. Reason could be the inability to acclimatize the microbes to the toxic environment.

Subsequent operational techniques such as reduction of sludge age and feeding glucose and protein helped to achieve required MLSS of 10,000 $\underline{+}$ 1000 mg/L in the reactor. Reduction of sludge age effectively controlled the worm growth problem in the reactor.

Later the MLSS of the reactor increased up to 23,000 mg/L indicating presence of microbes acclimatized to the toxic environment. At this stage the foaming was observed to be less when compared to the early unstable stages. So it could be concluded that foaming becomes less due to reduction of death of microbes as a result of acclimatization of microbes to the toxic environment.

4.3.2 MBR operation

Chemical cleaning was performed upon reaching the trans-membrane pressure to 70 kPa. Membrane clogging was observed in 34, 12, 15, 66 and 49 (not clogged at the instant of stopping the experiment) days intervals as seen in the figure 4.4. Data related to figure 4.4 are given in Table B-15 of Appendix B. Frequent membrane cleaning was needed during the early stages of MBR operation. The low membrane cycle of around 15 days was observed during this period as the reactor was unable to maintain the required MLSS. Subsequently the MBR cycle time improved to 66 days when the MLSS was above 10,000 mg/L. Low membrane cycle time can be related to loss of MLSS which occurred during the early stage of MBR operation, which was due to more biomass decay than growth which produced more extracellular polymeric substances (EPS) which is a main cause of membrane fouling. Membrane fouling can occur due to adsorption, pore blocking, precipitation, gel layer formation and bio film or cake formation (Mulder,1996 and Aim and Semmens, 2002) caused by deposited particles, colloids, emulsions, suspensions, macromolecules, salts etc. Acording to Aim and Semmens (2002) the main fouling agent is the colloidal fraction. Electrical properties of proteins, which are a main constituent of soluble EPS are sensitive to pH. Fouling is said to be minimized when pH is changed to isoelectric point of protein (i.e. when protein is electrically neutral).

Chemical cleaning was found to be effective in cleaning the fouled membranes. Resistance of cleaned membrane after each clean operation is shown in the Table 4.3. A sample calculation is shown in Appendix A. Cleaning membrane was done according to the membrane manufacturer's catalogue. The method is explained in section 3.3.2.5. The results were found to be better than those for the previous cleaning method, which used NaOH and HNO_3 suction through the membrane to clean it. Values in the table 4.3 could be compared with, resistance value1.58842 E 12 m^{-1} which was obtained by the previous cleaning method. Around 61% improvement in membrane resistance is noted with the new method.

MLVSS and MLSS variation of the MBR is shown in the figure 4.5. Data related to figure 4.5 are given in Table B-14 of Appendix B. Wide variation of MLSS and MLVS are observed due to unstable conditions in the MBR. MLVSS/MLSS ratio varied from 0.35 to 0.73 with an average of about 0.55. High MLVSS in sludge means more microbes. More MLSS indicates more particulate matter in sludge. Therefore higher the MLVSS/MLSS ratio, better the performance of activated sludge process. When compared with conventional activated sludge MBR the MLVSS/MLSS ratio of MBR sludge is low due to high content of particulate matter in sludge. This particulate matter is responsible for toxicity in MBR sludge.

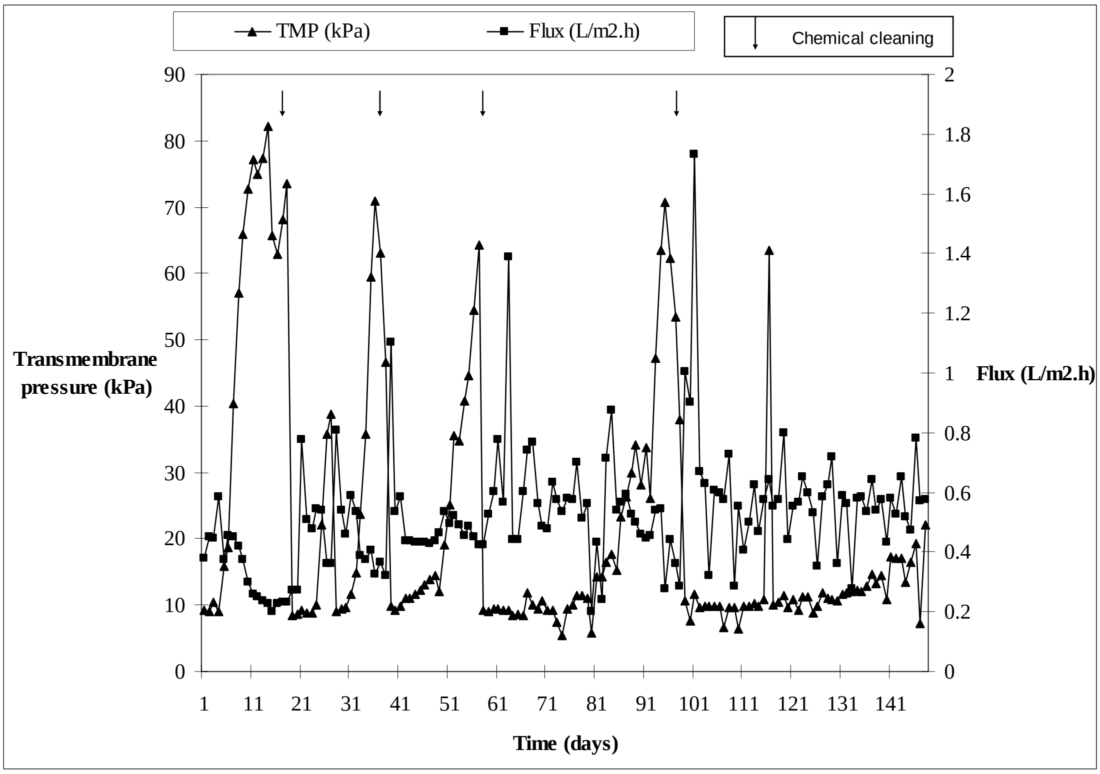


Figure 4.4 Membrane cycles

Table 4.3 Membrane resistance values upon each cleaning operation

Order of cleaning	Membrane resistance (m^{-1})
1	6.1218 E 11
2	7.49774 E 11
3	5.34135 E 11
4	5.89173 E 11

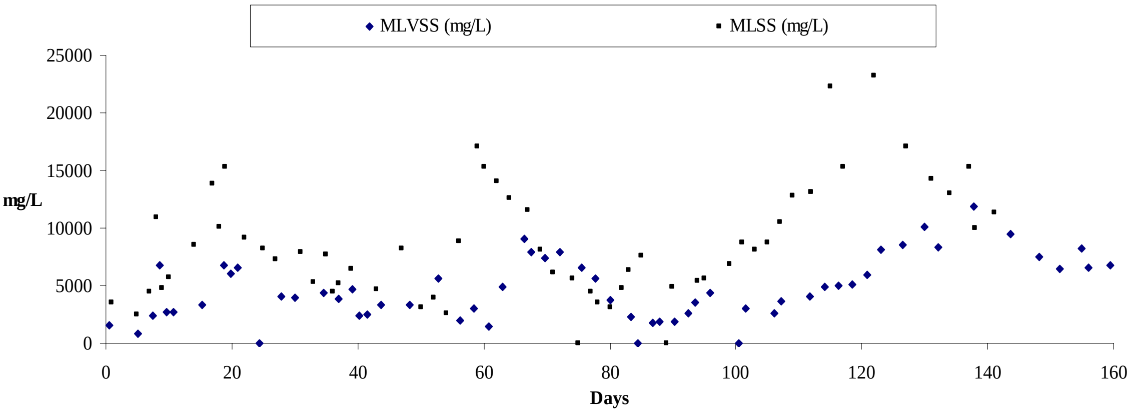


Figure 4.5 Variation MLSS and MLVSS of MBR with respect to time

4.3.3 Foaming

Foaming is one of the main problems encountered in MBR operation. Generally foaming in sewage treatment plants with activated sludge process occur due to abundance of filamentous micro organisms such as Actinomycetes which may contain Nocardia or Microthrix. But in this MBR experiment very much less filamentous organisms are observed. Therefore the foaming in MBR is different to the foaming in conventional activated sludge process. According to Nakajima (2003) foaming in MBR can occur due to protein and polysaccharides which suggests that extra-cellular polymeric substances (EPS) are the reason for foaming in MBR. EPS are product of cell decay and are absorbed by MLSS. As only free EPS contribute to foaming, addition of MLSS helps to reduce free EPS. Therefore the MLSS recirculation used to control the growth of higher species of micro organisms is also helping to reduce EPS thus reducing foaming. Also EPS is responsible for membrane fouling. This suggests that there is a relationship among Foaming, EPS and membrane fouling.

4.3.4 MBR efficiency

BOD_5 of MBR influent is within the range 2,000 to 3,500 mg/L which means organic loading is in the range of 2 to 3.5 $kg/m^3/d$. Also the sludge loading or F/M ratio is in the range of 0.25-0.44 kg /kg.d for MLSS of 8,000 mg/L. The main parameter controlling the efficiency of activated sludge process is the F/M ratio. It is necessary to keep the F/M ratio low to have higher efficiency of biodegradation and low sludge production. As the influent concentration, flux and the volume of reactor are maintained constant the only way to increase the efficiency is the increase of MLSS. In MBR it is possible to increase MLSS concentration much better compared to the conventional activated sludge process.
MBR has an average COD removal efficiency of 71.5% according to the data on Table B.9 of Appendix B. BOD_5 removal rate of the MBR is about 90% to 96% according to the Table B.11 of Appendix B. In study by Wichitsathian (2004), COD removal of 75.6% and BOD_5 removal of 98% have been reported. According to Table B.10 average TKN removal efficiency is 35% where in Wichitsathian (2004) it has been 25%.

Overall COD removal efficiency of the system ammonia stripping combined with the MBR is 77% according to data from Table B.9 of Appendix B. This removal efficiency is achieved with low influent BOD_5/COD ratio in the range of 0.29-0.37. This indicates less substrate resulting in slow growth of microorganisms. This influent characteristic resulted in an average MLVSS/MLSS ratio of 0.55 in the reactor, a low value when compared with conventional activated sludge process, meaning less microorganisms and more particulate matter as implied by high COD.

4.3.5 Sludge properties

Physical and rheological properties, EPS related parameters, sludge volume index values of MBR sludge at different MLSS conditions encountered during the experiment are shown in Tables 4.4, Table 4.5 and Table 4.6 respectively.

MBR sludge is found to be not settling well. More turbidity is observed in the supernatant. In MBR, diluted sludge volume index (DSVI) remained at 25.3 mL/g at MLSS of 8,700 mg/L. Such low value is a characteristic of small aggregate sludge according to Jenkins et al. (2003). Normal activated sludge has SVI values of 80 to 120 mL/g. Sludge with SVI<70 could be a pin floc sludge in case of conventional activated sludge. Pin floc sludge is characterized by no filamentous organisms, small weak floc, turbid supernatant and low SVI. This definition fits well to the present MBR sludge as microscopic investigation indicated that there are very few filamentous bacteria, which are essential element to give a structure to flocs to make them stronger. However this categorization with respect to conventional activated sludge cannot be directly used to categorize MBR sludge. Reason being that MBR sludge is subjected to strong shear forces in the reactor due to high turbulence caused by aeration causing size of sludge particles to be smaller than those of conventional activated sludge.

Table 4.4 Physical and rheological properties of MBR sludge

Parameter	Results set I	Results set II	Results set III
MLSS (mg/L)	2,560	9,967	12,767
MLVSS (mg/L)	1,420	6,533	8,183
Viscosity (cp)	13.9	55.2	25.8
DSVI (mL/g)		25	19.7
CST (secs.)	103	1,141	4,525

Table 4.5 EPS related parameters of MBR sludge

Parameter	Results set I	Results set II	Results set III
EPS, Bound (mg/g VSS)	139.9	108.9	85.1
EPS, soluble (mg/L)	1,525	3,290	2,615
Bound protein (mg/g VSS)	108.2	86.7	54.5
Soluble protein (mg/L)	1253	2536	1751
Bound carbohydrate (mg/g VSS)	31.7	22.2	30.6
Soluble carbohydrate (mg/L)	271.7	754	864
Bound protein/carbohydrate ratio	3.4	3.91	1.78
Soluble protein/carbohydrate ratio	4.61	3.36	2.03

Table 4.6 Variation of SVI and DSVI with MLSS

MLSS (mg/L)	MLVSS (mg/L)	MLVSS/MLSS	SVI or ***DSVI***(mL/g)
5,283	3,850	0.73	36
7,733	4,700	0.61	24.5
8,700	5,100	0.59	*25.3*
9,967	6,533	0.66	*25*
12,767	8,183	0.64	*19.7*

Note: DSVI values are shown in italics.

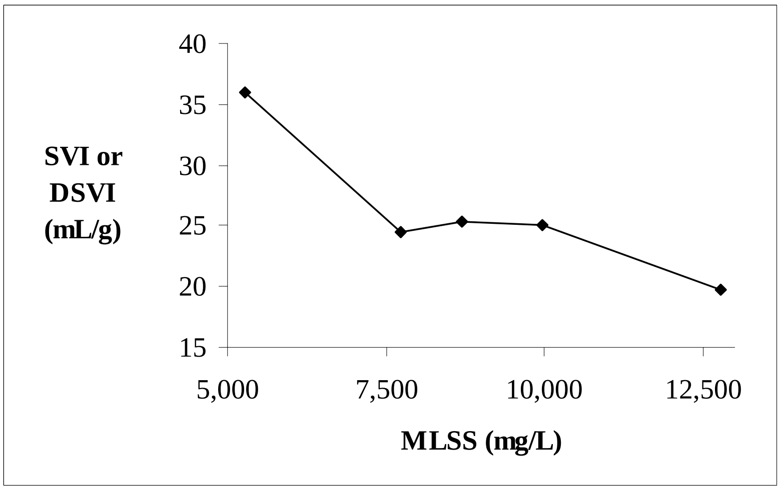


Figure 4.6 Variation of SVI or DSVI with MLSS of MBR

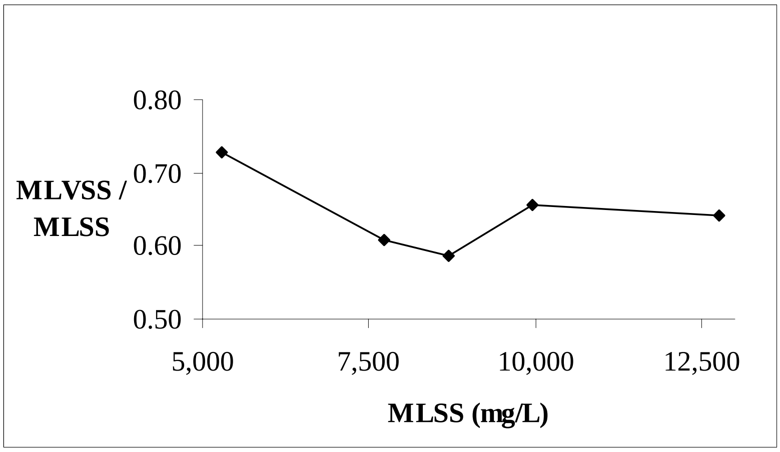


Figure 4.7 Variation of MLVSS: MLSS ratio with MLSS of MBR

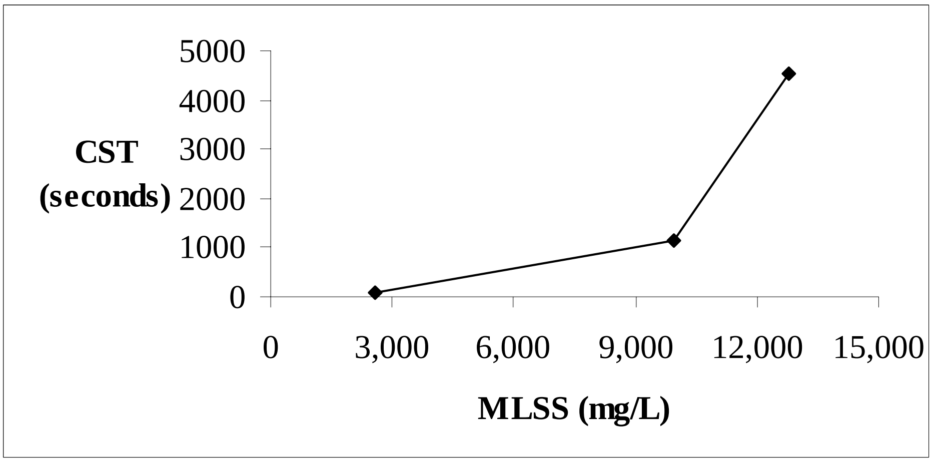


Figure 4.8 Variation of CST with MLSS of MBR

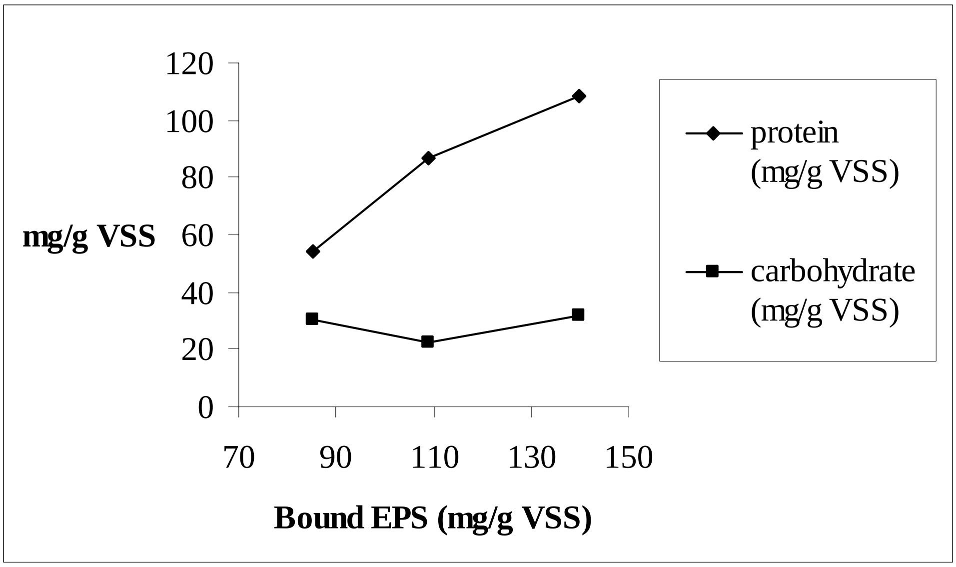


Figure 4.9 Variation of protein and carbohydrate contents in bound EPS

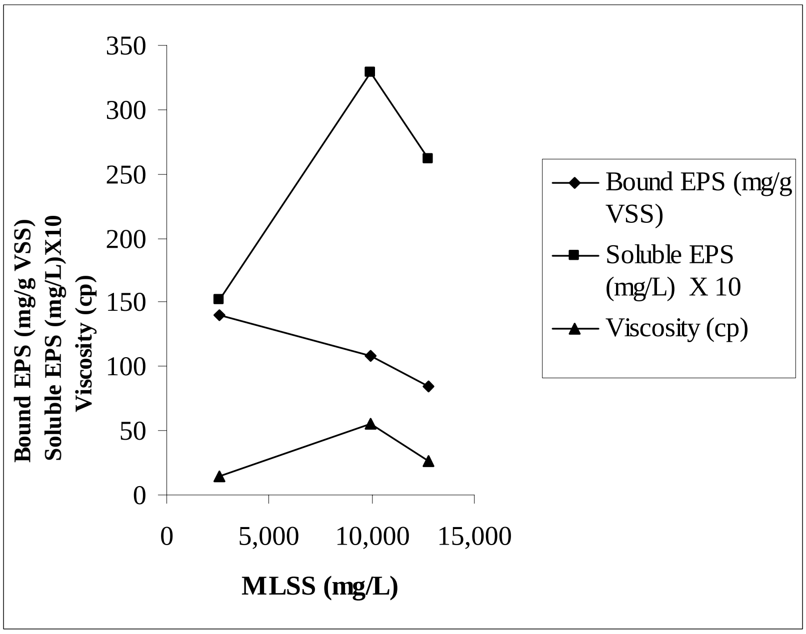


Figure 4.10 Variation of Bound EPS, soluble EPS and viscosity with MLSS of MBR

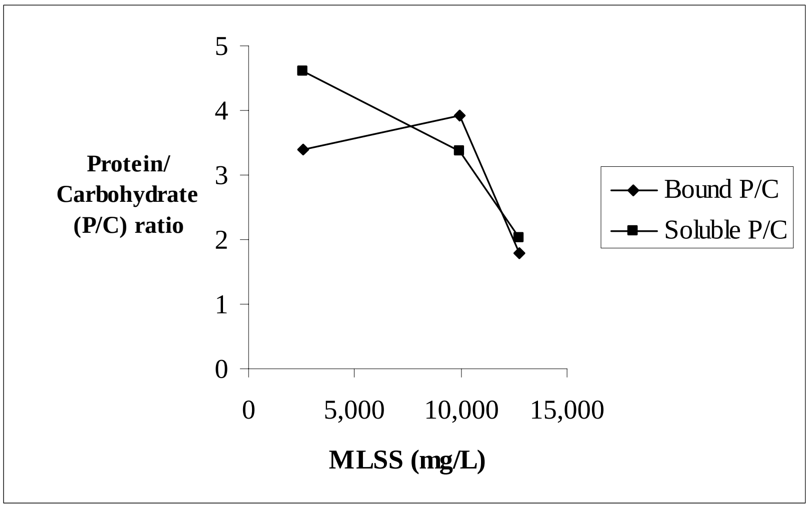


Figure 4.11 Variation of bound and soluble protein/carbohydrate ratio with MLSS of MBR

According to figure 4.9 and 4.11 it is seen that MBR sludge contains more protein than carbohydrate. Protein provides hydrophobic properties to sludge making better flocculation possible. But carbohydrate has got hydrophilic properties, which obstruct flocculation. Therefore protein in EPS is more important than carbohydrate in analyzing sludge settling characteristics. Figure 4.9 shows the increase of protein content with the increasing EPS content in MBR sludge. According to figure 4.11 a trend of reducing bound and soluble protein to carbohydrate ratio can be seen with increasing MLSS. This contributes to the reduction of hydrophobicity causing poor sludge settling. Further, the figure 4.10 shows a trend of increasing soluble EPS and reduction of bound EPS with increasing MLSS. This shows the conversion of bound EPS to soluble EPS with increase of MLSS. Also the trend of increase of viscosity shown in figure 4.10 confirms this conversion by means of increasing viscosity along with increase of MLSS. Figure 4.7 shows a reduction of MLVSS/MLSS ratio with increase of MLSS, which means relative “reduction” of microorganisms in sludge with increasing MLSS. The difficulty to dewater sludge at high MLSS is shown in figure 4.8 by increase of CST with increasing MLSS. Figure 4.6 shows the SVI or DSVI decrease with increasing MLSS. Although it appears to be an improvement of sludge settling, the fact that SVI values are DSVI for MLSS $\geq$ 8,700 mg/L means poor settling at high MLSS.

According to the above results increased MLSS creates more soluble EPS with less protein making sludge more viscous and making it difficult to settle and difficult to dewater.

4.4 Ozonation

Calibration of the ozonator was done in comparison to previous studies. Ozone generation varies with the voltage and oxygen flow rate. Ozone generator was calibrated to receive 75 mg/L ozone concentration value to be used for ozonation of MBR effluent. This ozone concentration has been established to be the optimum value, with respect to economy under previous work by Chaturapruek (2003).

4.4.1 Ozone in gas phase

Ozone demand and ozone concentration were calculated using the equations 3.3 and 3.4. The ozone concentration of 76 mg/L was obtained for oxygen flow rate of 0.6 L/min and voltage of 180 volts. Other ozone concentrations are shown in tables C-1, C-2, C-3 and C-4 of Appendix C.

4.4.2 Ozone in liquid phase

A standard curve was developed to measure the ozone concentration in the liquid phase as per 3.4.1.1 (b) is shown in figure 4.12. Sample of 5 mL mixed with neutral KI solution 5 mL to make 10 mL can be used to observe absorbance to get the ozone concentration in liquid phase using this standard curve. Curve data are given in Table C-5 of the Appendix C.

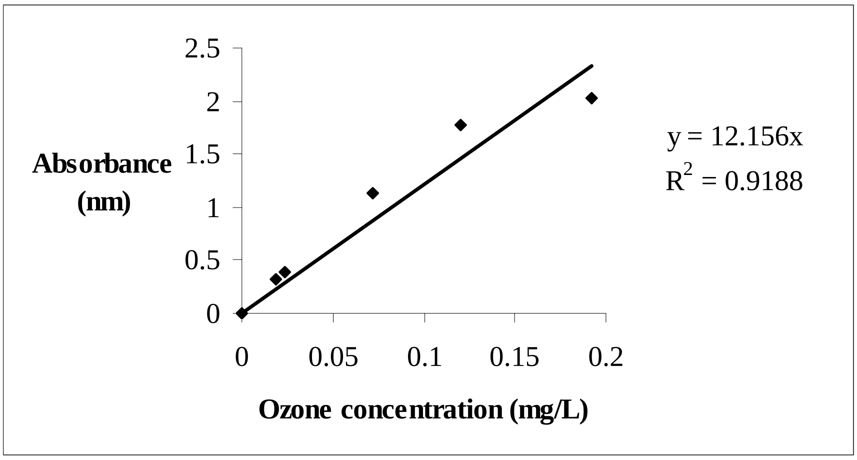


Figure 4.12 Calibration curve for determination of ozone concentration in liquid phase

4.4.3 Ozonation of MBR effluent

MBR effluent was ozonated at 75mg/L ozone concentration for 15, 30, 45 and 60 minutes and COD, BOD_5 and Color were measured to observe the effect of ozonation. Figures 4.13 and 4.14 show the COD variation due to ozonation. pH variation occurred during ozonation is shown in the figure 4.15. Figures 4.16 and 4.19 show the color variation. Figure 4.17 shows BOD_5 variation and the variation of BOD_5/COD ratio is shown in figure 4.18. Analytical data related to figures 4.13, 4.14, 4.15, 4.16, 4.17 and 4.18 are given in Table C-6, Table C-7, Table C-8 and Table C-9 of Appendix C.

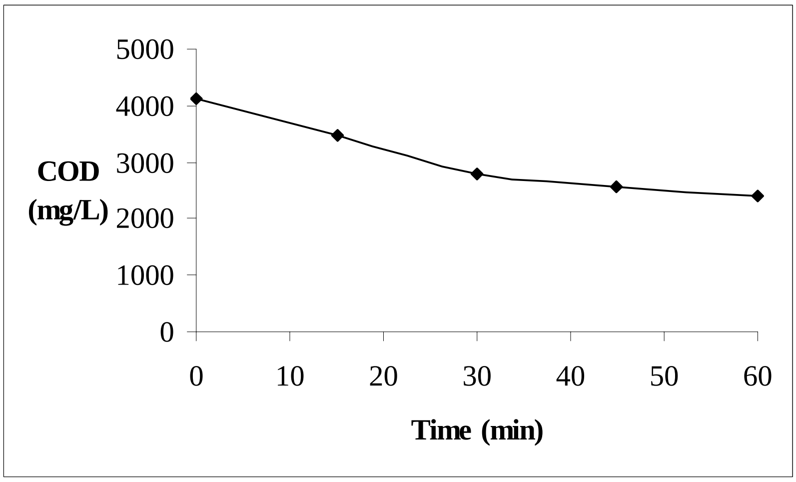


Figure 4.13 Variation of COD with time for ozone concentration 75 mg/L

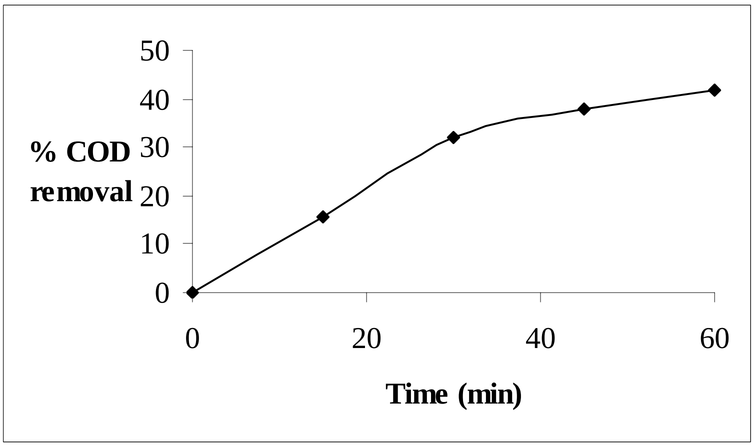


Figure 4.14 Variation of COD removal efficiency with time for ozone concentration 75 mg/L.

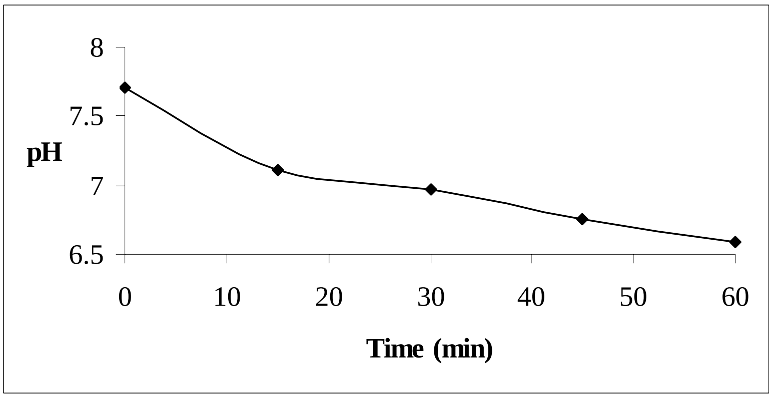


Figure 4.15 Variation of pH with time during ozonation at ozone concentration 75 mg/L

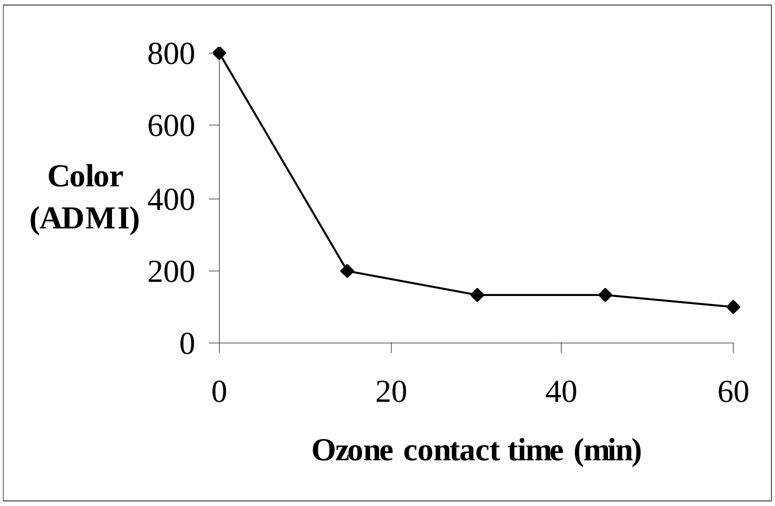


Figure 4.16 Variation of color with time for ozone concentration 75 mg/L

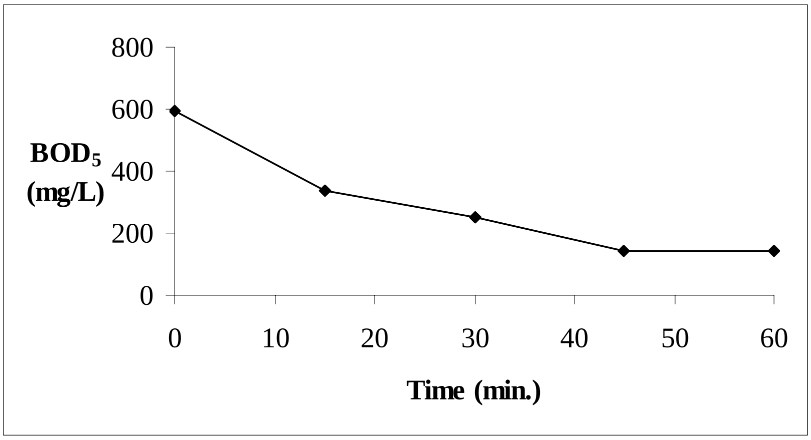


Figure 4.17 Variation of BOD_5 with time for ozone concentration 75 mg/L

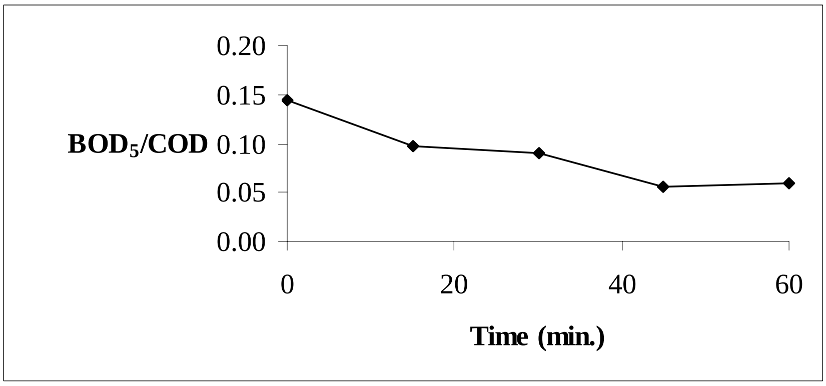


Figure 4.18 Variation of BOD_5 / COD ratio with time for ozone concentration 75 mg/L

Figure 4.19 Color change of MBR effluent during ozonation at 75 mg/L for 0, 15, 30, 45 and 60 minutes

According to above results, about 32% of COD is removed within 30 minutes. Also 57% of BOD_5 removal and 83% color removal took place during this period. As the COD and color values reached constant after 30 minutes, the optimum ozone contact time is considered as 30 minutes. Biodegradability measured as BOD_5 /COD ratio decreased from 0.14 to 0.09 in 30 minutes of ozonation of MBR effluent.

COD and BOD_5 reduction is due to oxidation caused by ozone. It is noted that the biodegradability is reduced to value which cannot be treated alone by biological process. Very high color removal is observed due to oxidation of dissolved organic carbon.

4.5 Molecular weight cut off (MWCO) study

Initial test on filtration of MBR effluent with 100 kDa ultra filtration membrane resulted in only 65 mL permeate out of 200 mL of MBR effluent filtered which was 32.5% passing in stirred filtration at 2 bar for 30 mins. Also MBR effluent with 10 kDa filtration gave 21 mL permeate out of 200 mL of MBR effluent filtered which was 10.5% passing in non stirred filtration at 2 bar for 30 mins. As the percentage volume passing was low to continue cutoff with finer membranes, it was decided to use effluent diluted with DI water to standardize MWCO experiment.

4.5.1 Standardization of MWCO study

Initially different dilutions of MBR effluent were prepared with 75 mL, 100 mL, 125 mL and 150 mL of sample mixed with DI water to make the total volume of 200 mL. Subsequently MWCO was done through a 100 kDa membrane at 2 bar pressure upto 30 mins. Common influent COD prior to dilution and permeate COD in each case were measured. Test was performed for both stirred and non stirred cases. Relevant data are shown in Appendix D.

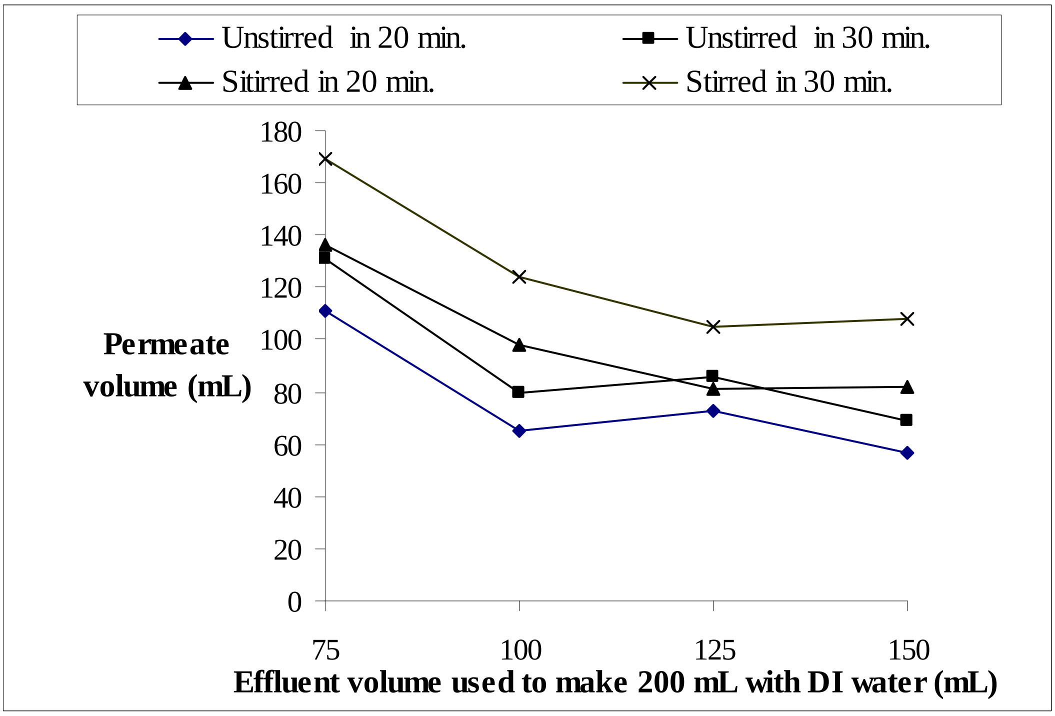


Figure 4.20 Permeate volumes received for different durations in MWCO by 100 kDa membrane for 200 mL of diluted MBR effluent solution

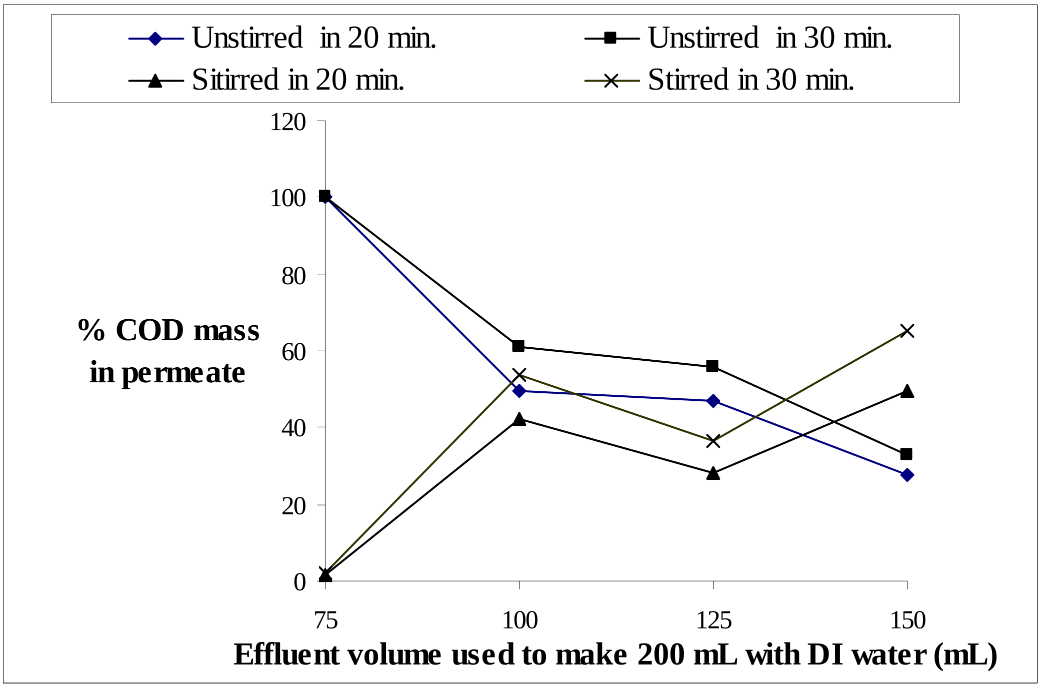


Figure 4.21 % COD mass found in permeate for different durations in MWCO by 100 kDa membrane for 200 mL of diluted MBR effluent solution

According to figure 4.20, stirring made the filtration better by giving filtrate volume more than 50% when compared with the non stirred test. 30 minutes filtration gave better outcome than 20 minutes. Filtration was not directly proportional to the dilution. In figure 4.21, it is seen that stirred test shows a trend of increasing COD mass in permeate with increasing concentration of the influent solution. In the non stirred test an opposite behavior of reducing the COD mass in permeate with increasing concentration of the effluent solution is observed. It is seen that these trends cross each other around 50% dilution. At this point the figure 4.20 shows that a permeate volume of more than 50% is achieved by stirred test in 30 minutes.

This leads to the conclusion of standardization of MWCO experiment to 2 bar pressure, 200 mL sample of 1:1 dilution with DI water and 30 min duration of filtration.

4.5.2 Molecular weight cutoff of MBR influent, MBR effluent and ozonated MBR effluent.

Results of the standardized MWCO batch test performed on MBR influent, MBR effluent and ozonated MBR effluent with 100 kDa, 50 kDa, 10 kDa and 5 kDa membranes are discussed. COD and TOC of initial influents, retentates of each membrane and final permeates were tested along with the volumes of each category. Detailed results are given in Appendix D.

According to figure 4.22 MBR influent contains only molecules > 100 kDa and < 5 kDa. The smaller fraction is about 18% of total volume. An additional fraction of molecules in 5 - 10 kDa range is observed in MBR effluent. Biological process in the reactor is the reason for this change. Upon ozonation of MBR effluent, this fraction shows an increase of about three folds. Also another molecule fraction in the range 10 – 50 kDa is seen to be generated after ozonation. It is seen that all new fractionations has occurred by conversion of > 100 kDa volume fraction. Figures 4.23 and 4.24 show, TOC and COD fractionation follow similar trend. But in ozonated effluent, a relative difference between TOC mass and COD mass is seen. That is COD mass depends more on >100 kDa fraction than TOC mass. The reason might be the >100 kDa fraction is rich in compounds with inorganic carbon than organic carbon.

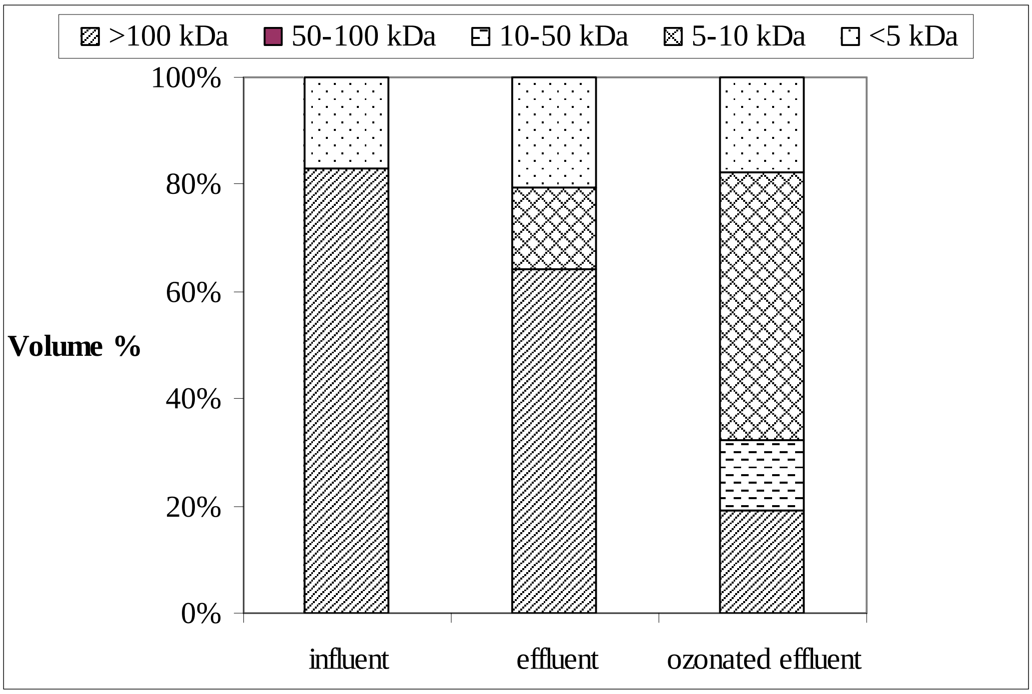


Figure 4.22 Volume balance of MBR influent, effluent and ozonated effluent

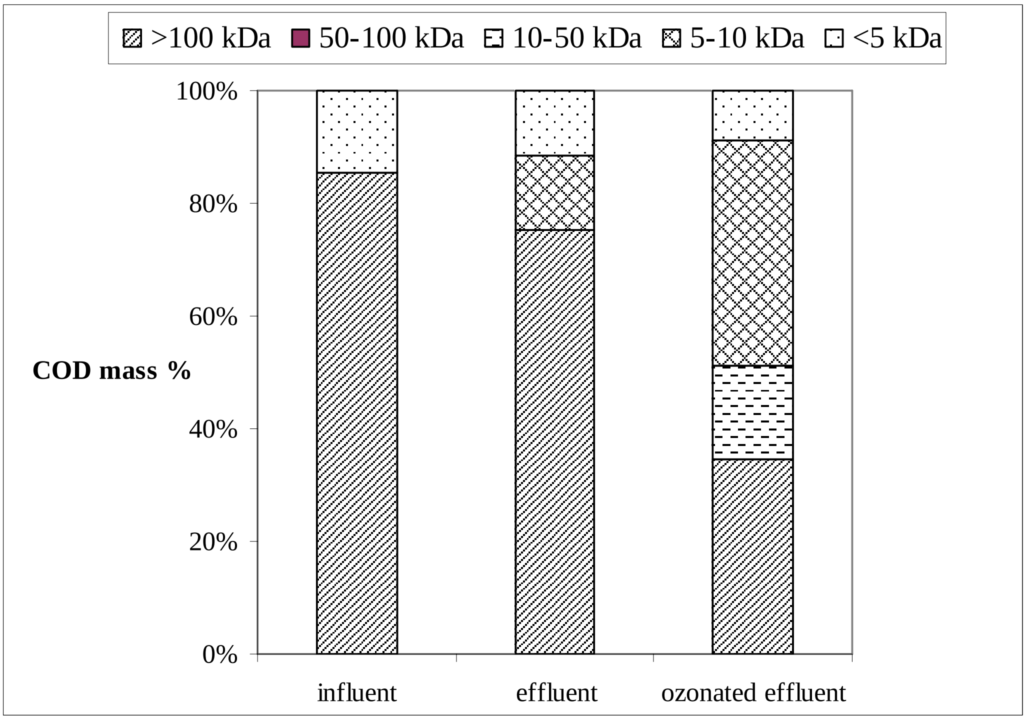


Figure 4.23 COD mass balance of MBR influent, effluent and ozonated effluent

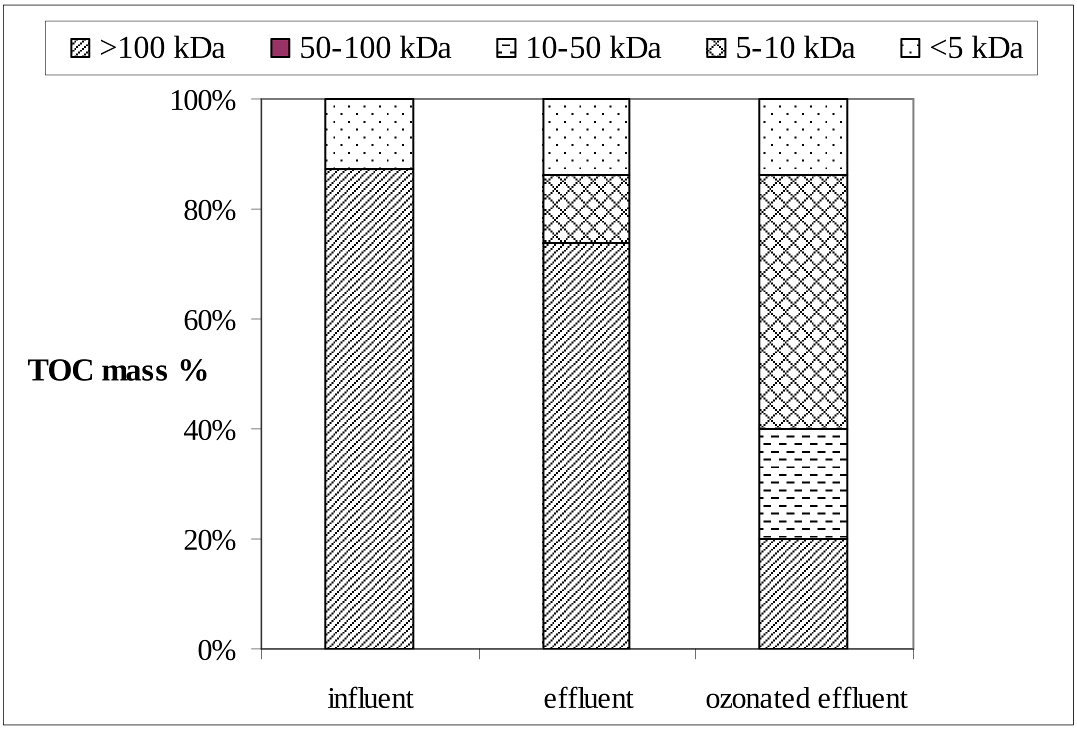


Figure 4.24 TOC mass balance of MBR influent, effluent and ozonated effluent

4.5.2.1 Variation of membrane resistance during the batch test

Each filtration test was performed using a new membrane. Membrane resistance was measured before and after filtration. Percentage increase of membrane resistance upon filtration of MBR influent, MBR effluent and ozonated MBR effluent is shown in Table 4.7.

Table 4.7 Variation of membrane resistance (m^{-1}) during batch test

Membrane size (kDa)	New membrane	After filtering MBR Influent (% increase of resistance)	After filtering MBR Effluent (% increase of resistance)	After filtering ozonated MBR Effluent (% increase of resistance)
100	3.48722 E11	-	-	-
50	1.74316 E12	2.67113 E 12 (53)	2.45639 E12 (41)	2.57639 E12 (48)
10	3.67805 E12	4.33263 E 12 (18)	4.10211 E12 (12)	4.37865 E 12 (19)
5	1.15227 E13	1.41189 E 13 (23)	1.54611 E13 (34)	1.84155 E 13 (60)

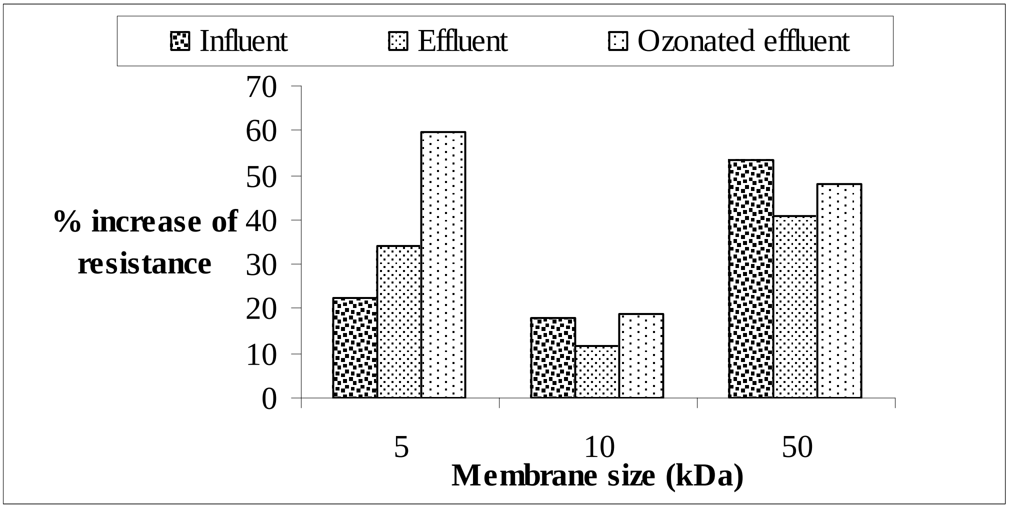


Figure 4.25 Percentage increase of membrane resistance on different membrane sizes due to filtration of influent, effluent and ozonated effluent

According to figure 4.25 the maximum percentage of increase of the membrane resistance occurred in the 5 kDa membrane when ozonated effluent was filtered. Ozonated MBR effluent always clogged the membranes more than all other test conditions. This suggests that the new molecules generated by ozonation have more contribution on membrane clogging.

The increase of membrane resistance is a result of different phenomena such as pore blocking, adsorption and gel layer formation. The main phenomena of membrane clogging, gel layer formation, is delayed by stirring action during experiment which reduces concentration polarization of the molecules which is the preliminary step of gel layer formation.

4.5.3 Molecular weight cutoff study of MBR influent and effluent under continuous recycle study

MBR effluent was ozonated for 30 minutes at 75 mg/L ozone concentration. This ozonated effluent was recycled into the MBR mixing at 1:1 ratio with supernatant of ammonia stripped leachate.

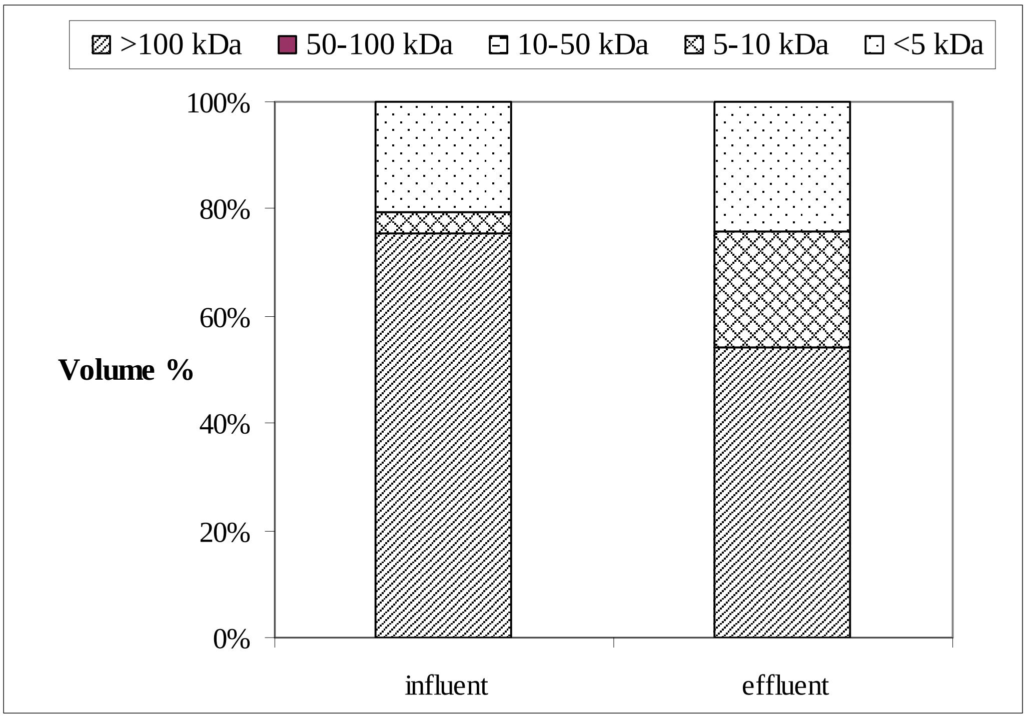


Figure 4.26 Volume balance of recycled MBR influent and effluent

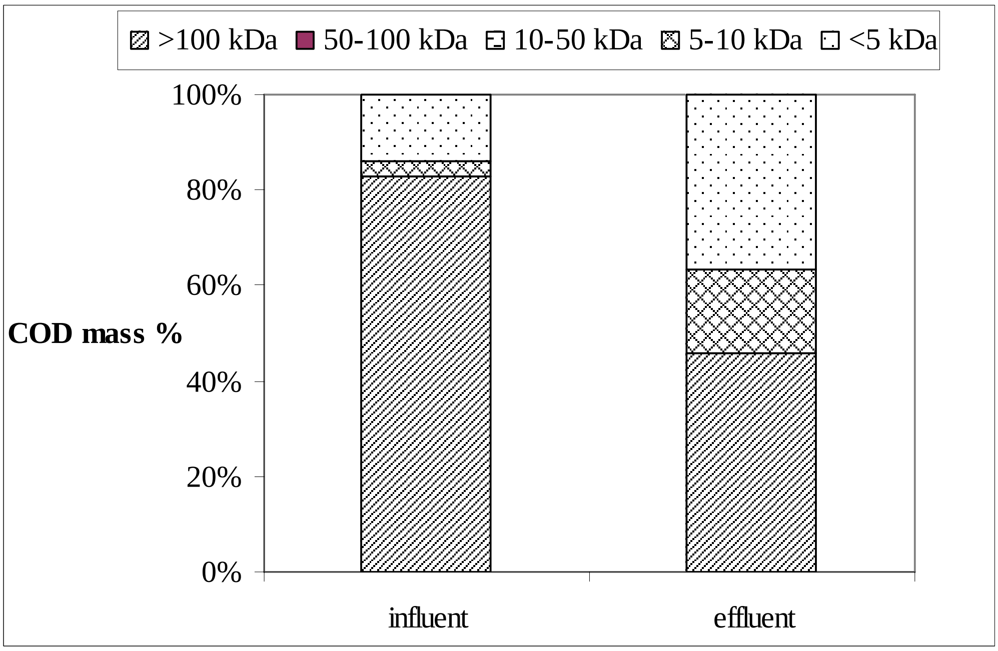


Figure 4.27 COD mass balance of recycled MBR influent and effluent

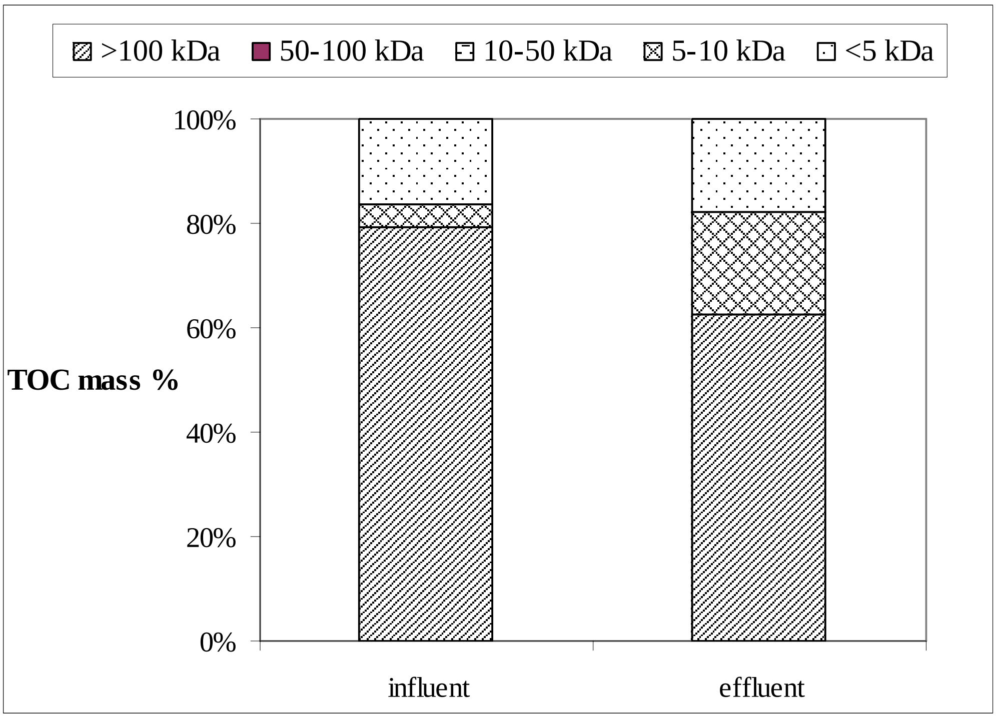


Figure 4.28 TOC mass balance of recycled MBR influent and effluent

Figure 4.26 shows the volumetric fractionation of the influent and effluent. It is seen that the >100 kDa fraction in the effluent remain at about 50%. COD and TOC fractionation followed similar patterns as shown in figure 4.27 and figure 4.28. The molecular weight fraction <5 kDa remained constant except for COD. There was an increase in 5-10 kDa molecular weight fraction due to degradation in MBR by the biological process.

4.5.4 Comparison of molecular cut off study results of MBR effluent ozonation and recycle of ozonated MBR effluent

The low volume of >100 kDa fraction seen in ozonated effluent of figure 4.22 has increased in the recycled effluent according to figure 4.26. This can be attributed to the mixing ozonated leachate with ammonia stripped leachate which increases the mixed nature of molecules. The fraction < 5 kDa remained almost constant in both cases which suggests that it is a non bio degradable fraction. Also the 10-50 kDa molecule fraction seen in figure 4.22 has been disappeared in figure 4.26. As this has happened during 1:1 mixing stage well before the bioreactor, ionic strength properties may be the reason for this behavior by causing this smaller molecular fraction getting attached to stripped leachate molecules changing the apparent molecular weight. This change of apparent molecular weight due to molecular rearrangement may be the reason for the disappearance of 10-50 kDa molecular weight fraction.

4.5.5 Changes in MBR efficiency due to recycled ozonated effluent

Table 4.8 Change in MBR efficiency in terms of COD due to recirculation of ozonated MBR effluent

	Influent COD (mg/L)	**Effluent COD (mg/L)**	**MBR efficiency %**
Before ozonation	5,638	3,885	31
After continuous ozonation	4,952	2,667	46

Table 4.9 Change in MBR efficiency in terms of TOC due to recirculation of ozonated MBR effluent

	Influent TOC (mg/L)	**Effluent TOC (mg/L)**	**MBR efficiency %**
Before ozonation	1,888	1,296	31
After continuous ozonation	1,560	988	37

Table 4.10 Change in MBR efficiency in terms of BOD_5 due to recirculation of ozonated MBR effluent

	Influent BOD_5 (mg/L)	**Effluent BOD_5 (mg/L)**	**MBR efficiency %**
Before ozonation	1,241	85	93
After continuous ozonation	900	150	83

Table 4.11 Change in biodegradability due to recirculation of ozonated MBR effluent

	Influent BOD_5/COD ratio	**Effluent BOD_5/COD ratio**
Before ozonation	0.22	0.02
After continuous ozonation	0.18	0.09

According to Table 4.8 the re-circulated effluent increased MBR efficiency from 31% to 46% in terms of COD. Efficiency improvement in terms of TOC is from 31% to 37% according to Table 4.8. According to Table 4.10 continuous recirculation dropped BOD removal efficiency from 93% to 83%. Table 4.11 shows a slight drop in biodegradability in terms of BOD_5 / COD in influent from 0.22 to 0.18. Low effluent BOD_5 /COD ratios of 0.02 and 0.09 show, that the MBR is treating the influent to its maximum possible levels.

The overall drop of MBR efficiency observed may be due to inhibitory effects of MBR sludge. However ozonation is found to slightly increase the treatment efficiency of the MBR.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

1. Ammonia stripping process was capable of removing 59± 14 % of ammonia on average. The result is comparable with the previous study. During this process an average COD reduction of 36% was observed. Also the BOD_5/COD ratio was found to drop from 0.42 to 0.37.

2. Average MBR efficiency with respect to COD removal was 71.5% and the average overall COD removal of the ammonia stripping combined with MBR was 77%. Average MBR efficiencies of BOD_5 and TKN removal were 93% and 36% respectively.

3. The increase of MLSS in MBR sludge made it difficult to settle. MBR sludge is characterized by average low MLVSS/ MLSS ratio on the range of 0.55 when compared with conventional activated sludge. Shifting SVI value to DSVI with the increase of MLSS during the experiment indicates difficulty in sludge settling. Also the soluble EPS in sludge increased with increase of MLSS while bound EPS dropped. Both bound and soluble Protein/ Carbohydrate ratio dropped with the increase of MLSS. As protein is responsible for sludge hydrophobicity, which promotes sludge settling, the above result implies that the difficulty in settling sludge increases with the increase of MLSS.

4. Increase of MLSS of MBR sludge made it difficult to dewater as shown by increase of CST.

5. Ozone contact time required of ozonation of MBR effluent was found to be 30 minutes. Ozonation caused about 32% reduction of COD and 57% of BOD_5 reduction in MBR effluent. The remaining COD can be believed to be consisting of refractory organic compounds. Also a drop in BOD_5/COD ratio from 0.14 to 0.09 was observed. The value 0.1 is said to be the minimum ratio of BOD_5/COD that could be treated by MBR activated sludge process. Although ozonation generated smaller molecular fractions in MBR effluent, both BOD_5 and COD dropped due to strong oxidative character of ozone.

6. Ozonation was very much effective in color removal of MBR effluent due to its high oxidative property. 83% color removal was shown during the experiment.

7. Molecular weight cut off study was standardized by using 1:1 dilution with DI water and nitrogen gas of 2 bar pressure on 200 mL initial volume on stirred module with 30 minutes filtration. Standardization made interpretation of the results more precise and easy to compare with other results.

8. Molecular weight cut off upon ozonation revealed that MBR effluent had about 20% refractory fraction after ozonation. MBR could not treat this fraction. In this case MBR influent had only two molecular fractions, > 100 kDa and < 5kDa. MBR effluent showed creation of a fraction 5-10 kDa out of influent fraction >100. This fraction increased three folds along with creation of another fraction of 10-50 kDa

upon ozonation. This shows generation of new products of low molecular weight during MBR biological process and more such products during ozonation.

9. The 5-10 kDa molecular weight fraction generated in item 8 above showed the highest percentage increase of membrane resistance out of all the membranes used in the experiment indicating a molecular character of that fraction, capable of making a strong gel layer.

10. Treatment of recycled ozonated MBR effluent in 1:1 ratio continuously in MBR showed reduction of >100 kDa molecular fraction by about 20% converting to 5-10 kDa fraction.

11. Continuous recycled MBR efficiency in terms of COD removal improved from 31% before recycle to 46% after recycle. TOC removal also increased from 31% to 37%. BOD_5 removal dropped from 93% to 83%. This concludes that there is an overall MBR efficiency improvement of low magnitude due to continuous recirculation of ozonated MBR effluent.

5.2 Recommendations

1. Low BOD_5/COD ratio of the MBR influent in 0.29-0.37 range and low MLVSS/MLSS ratio of 0.55 in the reactor sludge suggest the presence of refractory organic compounds in leachate which are being transferred to the reactor sludge. Although this could be considered as a means of eliminating such compounds from the effluent to be discharged to the environment, question of treatment of wasted sludge remains. It is proposed that sludge ozonation can help to oxidize such compounds in sludge. Therefore further studies on sludge ozonation and recirculation are recommended.

2. An oxygen uptake rate study of MBR sludge could be a part of the study mentioned in item 1 above to compare oxygen uptake rate and growth parameters with those of conventional activated sludge.

3. Molecular weight of protein related molecules could vary according to changes of ionic strength of solution and pH. As this could affect the results of molecular weight cut off study, further studies on changes in MWCO results by pH variations are recommended.

4. Identification of predominant compounds found in each molecular weight fraction of MWCO study could lead to better understanding of possibilities for further treatment of effluent.

5. Continuous recirculation of ozonated MBR effluent could be performed for a period of 3 days only due to limitations on study time. This experiment needs to be done for a longer period with different recycle ratios along with precisely monitored ammonia stripping process for well establishment of the results.

References

Agren, S. (2003). The possible similarity between organic substances in leachates and forest waters. Retrieved from the Ragnat Sellberg Foundation web site http://rss-fukia.org/pdf/Possible_Similarity.pdf, in December 2003.

Ahn, K.H., Park K.Y., Maeng, S.K., Hwang, J.H., Lee, J.W., Song, K.G. and Choi, S. (2002). Ozonation of wastewater sludge for reduction and recycling. *Water Science & Technology,* 46(10), 71-77.

Ahn, K.H., Yeom, I.T., Park, K.Y., Maeng, S.K., Lee, Y.,Song, K.G. and Hwang, J.H. (2003). Reduction of sludge by ozone treatment and production of carbon source for denitrification. *Korea institute of Science & Technology.*

Andersen, K and Sigvardsen, L. (1996). Experiences with sludge setleability in different process alternatives for nutrient removal. *Water Science & Technology*, 33 (12), 137-146.

APHA, AWWA, WPCF, 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition, Washington DC, USA.

Baig, S. & Liechti, P.A. (2001). Ozone treatment for biorefractory COD removal. *Water Science & Technology*,43 (2), 197-204.

Bura, R., Cheung, M., Liao, B., Finlayoson, J., Lee, B.C., Droppo, I.G., Leppard, G.G., and Liss, S.N.(1996). Composiyion of extracellular polymeric substances in the activated sludge floc matrix, *Water Science and Technology*, 37(4-5), 325-333.

Chaturapruek, A. (2003). Ozonation combined with membrane bio-reactor for landfill leachate treatment, Master Thesis, AIT.

Chen, T.K., Ni, C.H., Chen, J.N. & Lin, J.(2003). High-strength nitrogen removal of opto-electronic industrial wastewater in membrane bioreacotor- a pilot study, *Water Science & Technology*, 48(1), 191-223.

Cossu, R., Polcaro, A.M., Lavagnolo, M.C. and Palmas, S.(2003). Treatment of MSW landfill leachate by electrochemical oxidation. Retrieved from the web site http://www.sardiniasymposium.it/papermodel.pdf, in December 2003.

Drouiche, H., Lounici, H., Mameri, N., Piron, D.L. & Kharroune, M. (2001). Ulilization of factorial experiments for the UV/H_2O_2 process in a batch reactor, *Water SA*, 27(4), 551-557. Retrieved from the web site http://www.wrc.org.za/publications/watersa/2001/October/1360.pdf, in December 2003.

Eikelboom, D.H. (2000). Process control of activated sludge plants by microscopic investigation, IWA publishing, London, United Kingdom.

Erdincler, A. and Vesilind, P.A.(2000). Effect of sludge cell disruption on compactibility of biological sludges, *WaterScience &Technology,* 42(9), 119-126.

Fletcher, I.J. and Ashbee, E. (1994). Ammonia stripping for landfill leachate treatment- A review, Horan, N.J. & Lowe, R. (Eds.), Nutrient removal from waste water, Technomic Publishing Company, Inc., 109-117.

Guan, R., Amal, R. & Waite, T.D. (2003). Effects of floc size & structure on biosolids on capillary suction time. *Water Science & Technology*, 47 (12), 255-260.

Gunten, U.V., (2003). Ozonation of drinking water: Part I. Oxidation kinetics and product information. *Water Research*, 37, 1443-1467.

Hanel, K.(1988). Biological treatment of sewage by the activated sludge process, Ellis Horwood Limited, Chichester, England.

Hayer, K.U. and Stegman, R. (2003). Leachate management: leachate generation, collection, treatment and costs. Retrieved from the Ingenieurburo fur Abfallwirtschaft website, http://www.ifas-hamburg.de/index_engl.htm, in December 2003.

Jenkins, D., Richard, M.G. and Daigger, G.T.(2003). Manual on the causes and control of activated sludge bulking and foaming, USA

Jimenez, D.B.M., Narbaitz, R.M., Matsuura, T., Chowdhury, G., Pleizier, G. and Santerre, J.P. (2004). Influence of processing conditions on the properties of ultrafiltration membranes, *Journal of Membrane Science*, 231 (1-2), 209-224.

Kamiya, T. & Hirotsuji, J. (1998). New combined system of biological process and intermittent ozonation for advanced wastewater treatment. *Water Science & Technology*, 38 (8-9), 145-153.

Kim, J.S. & Lee, C.H. (2003). Effect of powdered activated carbon on the performance of an aerobic membrane bioreactor: comparison between cross-flow and submerged membrane systems. *Water Environment Research*, 75(4), 300-307.

Lee, Y., Cho, J., Seo, Y., Lee, J.W, Ahn, K.H.(2002). Modeling of submerged membrane bioreactor process for wastewater treatment. *Desalination*, 146, 451-457.

Lema, J.M., Mendez R. and Blazquez R., (1988). Characteristics of Landfill leachates and alternatives for their treatment: *A review, Water, Air and Soil Pollution*. 40, 223-250.

Liu, Y & Fang, H.P. (2003). Influences of extracellular polymeric substances (EPS) on flocculation, Settling and dewatering of activated sludge. *Critical Reviews in Environmental Science & Technology*, 33(3),237-273.

Marttinen, S.K. , Kettunen, R.H., Sormunen, K.M., Soimasuo, R.M. & Rintala, J.A. (2002). Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates. *Chemosphere*, 46, 851-858.

Metcalf and Eddy (2003). Waste water engineering treatment and reuse, McGraw Hill, USA.

Mudler, M. (1996). Basic principles of membrane technology, Kluwer Academic Publishers, The Netherlands.

Nakajima, J. (2003). Measurement of foam quality of activated sludge in MBR process. 9th IWA conference colloquium retrieved from the web site http://www.vscht.cz/tvp/9th_IWA_Conf/colloquium/Nakajima.pdf, in May 2004.

Sanin F.D. (2002). Effect of solution physical chemistry on the rheological properties of activated sludge, *Water SA*, 28(2), 207-211.

Setiadi, T. and Fairus, S. (2003). Hazardous waste landfill leachate treatment using an activated sludge-membrane system, *Water Science and Technology*, 48 (8) 111- 117.

Shechter, H. (1973). Spectrophotometric method for determination of ozone in aqueous solutions, *Water Research*, 7,729-739.

Staehelin, J. & Holgne, J. (1982). Decomposition of Ozone in water: Rate of Initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Technol*., 16, 676-681.

Thiel, D.J. (2002). Activated sludge, WEF manual of practice No. OM-9, Water Environmental Federation ,USA.

Urbain, V., Mobarry, B., Silva, V. de, Stahl, D.A., Rittmann, B.E., Manem, J. (1998). Integration of performance, molecular biology and modeling to describe the activated sludge process. *Water Science & Technology*, 37(3), 223-229.

Visvanathan, C., Aim, R.B. & Parameshwaran, K. (2000). Membrane separation bioreactors for wastewater treatment, *Critical Reviews in Environmental Science & Technology*, 30(1),1-48.

Wichitsathian, B. (2004). Application of membrane bioreactor systems for landfill leachate treatment. Phd. Dissertation, AIT.

Yoon, S.H., Kim, H.S. and Yeom, I.T. (2004). The optimum operational condition of membrane bioreactor(MBR): cost estimation of aeration and sludge treatment. *Water Research*, 38, 37-46.

Zamora,R.M.R, Moreno, A.D.,Valasquez, M.T.O de and Ramirez, M. (2000). Treatment of landfill leachates by comparing advanced oxidation and coagulation –flocculation processes coupled with activated carbon adsorption, *Water Science & Technology*, 41(1), 231-235

Zhou, H. & Smith, D.W. (2002). Advanced technologies in water & wastewater treatment, *Environ. Eng. Sci.* 1:247-264, Retrieved from the web site http://www.environmental-center.com/magazine/nrc/jees/s02-020.pdf , in November 2003.

APPENDICES

APPENDIX C

Results of ozonation study

Appendix C: Results of ozonation study

1. Ozone in gas phase

Table C-1. Ozone concentration in gas phase at oxygen flow rate = 0.6 L/min

Voltage (V)	**Contact time (min)**	**mL of $Na_2S_2O_3$**	**Ozone demand (mg/min)**	**Ozone concentration (mg/L)**
200	1	5.1	38.25	63.75
	3	7.5	18.75	31.25
	5	26.8	40.20	67.0
Average ozone concentration				54.0

Table C-2. Ozone concentration in gas phase at oxygen flow rate = 0.6 L/min

Voltage (V)	**Contact time (min)**	**mL of $Na_2S_2O_3$**	**Ozone demand (mg/min)**	**Ozone concentration (mg/L)**
200	1	5.8	43.5	72.5
	3	3.95	31.5	52.5
	5	23	34.5	57.5
Average ozone concentration				60.8

Table C-3. Ozone concentration in gas phase at oxygen flow rate = 0.2L/min

Voltage (V)	**Contact time (min)**	**mL of $Na_2S_2O_3$**	**Ozone demand (mg/min)**	**Ozone concentration (mg/L)**
180	1	2.2	16.5	82.5
	3	6.1	15.25	76.25
	5	9.6	14.4	72
Average ozone concentration				76.91

Table C-4. Ozone concentration in gas phase at oxygen flow rate = 0.6L/min

Voltage (V)	**Contact time (min)**	**mL of $Na_2S_2O_3$**	**Ozone demand (mg/min)**	**Ozone concentration (mg/L)**
180	1	6.05	45.375	75.625
	3	18.1	45.25	75.42
	5	30.9	46.35	77.25
Average ozone concentration				76.09

2. Ozone in liquid phase

Table C-5 Calibration curve using spectrophotometer for ozone in liquid phase

Ozone concentration (mg/L)	Absorbance (nm)
0	0
0.0192	0.328
0.024	0.391
0.072	1.136
0.120	1.768
0.192	2.021
0.288	1.998

3. Ozonation of MBR effluent

Table C-6 Ozonation of MBR effluent

Ozone contact time (min.)	COD (mg/L)	% COD removal
0	4120	0
15	3480	16
30	2800	32
45	2560	38
60	2400	42

Table C-7 Variation of pH with ozonation of MBR effluent

Ozone contact time (min.)	pH
0	7.71
15	7.11
30	6.97
45	6.76
60	6.59

Table C-8 Variation of BOD_5/COD during ozonation of MBR effluent

Time (min.)	COD (mg/L)	BOD_5 (mg/L)	BOD_5/COD
0	4120	593	0.14
15	3480	339	0.10
30	2800	254	0.09
45	2560	141	0.06
60	2400	141	0.06

Table C-9 Variation of color during ozonation of MBR effluent

Ozone contact time (min.)	**Color (ADMI)**
0	800
15	200
30	133
45	133
60	100

APPENDIX A

Sample Calculations

APPENDIX B

Results of ammonia stripping and MBR efficiency

Appendix B : Results of Ammonia stripping and MBR efficiency

1. Ammonia stripping experiment

Table B.1- Properties of raw leachate used in the experiment

Leachate sample	BOD_5 (mg/L)	COD (mg/L)	NH_4^+ N (mg/L)	pH	BOD_5/COD
Ram-Indra	60,700	69,667	448	3.8	0.87
Pathumthani	1,072	3,542	1,120	8.2	0.3

Table B.2- Test results on standardization of ammonia stripping

Sample		COD (mg/L)	BOD_5 (mg/L)	NH_4^+ N (mg/L)	pH
Mixed leachate		8,065	3,388	1,022	7.5
Supernatant of stripped leachate	2hrs	7,279	2,766	784	11.1
	4hrs	6,984	2,653	560	11.0
	5hrs	6,787	2,540	490	10.9

Table B.3- Test results on standardization of ammonia stripping, % removal efficiencies

Sample		COD	BOD_5	NH_4^+ N
Supernatant of stripped leachate	2hrs	9.7	18.4	23.3
	4hrs	13.4	21.7	45.2
	5hrs	15.8	25.0	52.1

Table B.4- Variation of BOD_5/COD with respect to stripping time

Stripping time (h)	BOD_5/COD
0	0.42
2	0.38
4	0.38
5	0.37

Table B.5 – Ammonia concentration (mg/L) in 5 h stripping process

Mixed leachate	After stripping process	% removal
1,064	784	26
1,176	392	67
1,022	490	52
1,974	812	59

Table B.6– COD concentration (mg/L) in 5 h stripping process

Mixed leachate	After stripping process	% removal
8,375	4,204	50
8,065	6,786	16
9,274	7,362	21
7,294	3,294	55

2. MBR efficiency

Table B.7 - MBR efficiency test

Sample	pH	BOD_5 (seeded) mg/L	BOD_5 (Non seeded) mg/L	COD mg/L	NH_4-N mg/L	TKN mg/L
I-before stripping	7.53-11.97	4,291	4,460	9,275	1,008	1204
II-after stripping	11.06	3,669	3,162	7,363	504	616
III-MBR Effluent	7.87			2,390	168	
IV-MBR Influent	7.86	2287	2000	6,886	308	
V- MBR Effluent	7.98	87	87		168	392

Table B.8 MBR efficiency as % removal of each category of Table B.7 above

	BOD_5	COD	NH_4-N	TKN
Ammonia stripping efficiency	29	26	69.4	48.8
MBR efficiency	97	65.3	45.5	36.4
Overall removal efficiency	98	74.2	83.3	67.4

Table B.9 MBR Efficiency in terms of COD removal

Ramindra Leachate (mg/L)	**Pathumthani Leachate (mg/L)**	**Mixed Leachate (mg/L)**	**After Stripping (mg/L)**	**MBR Effluent (mg/L)**	**MBR Efficiency**	**Overall Efficiency**	**MLSS (mg/L)**
			8,516	619	93%		
			10,839	1,084	90%		
			5,419	1,548	71%		
46,452	3,871						
54,109	6,109	12,800					
61,852	4,510	8,376					
			4,204	701	83%	92%	9,000
69,639	3,541						
		6,750					
59,328	3,648	7,680					
		9,275	7,363	2,390	68%	74%	6,420
			1,694	941	44%		4,783
			1,882				
79,585	3,554						
			6,750				
		13,377	5,508	1,574	71%	88%	4,500
90,843	6,030	15,074					
		7,294	6,902	3,294	52%	55%	4,916
	4,535		5,858	3,969	32%		6,916

Table B.10 MBR efficiency in terms of NH_3N removal & TKN removal

NH_3 N			**TKN**		
Influent (mg/L)	**Effluent (mg/L)**	**Efficiency (%)**	**Influent (mg/L)**	**Effluent (mg/L)**	**Efficiency (%)**
504	168	67			
308	168	45			
1,154	450	61			
812	140	83			
1,467	862	41	1,596	1,008	37
1,324	672	49	1,456	784	46
532	448	*16*	644	504	22

Table B.11 MBR efficiency in terms of BOD$_5$ removal

Influent (mg/L)	**Effluent (mg/L)**	**Efficiency %**
1,976	198	90
2,000	87	96
1,242	84.7	93

Table B.12 BOD$_{20}$ comparison with BOD$_5$

	BOD$_5$ (mg/L)		**BOD$_{20}$ (mg/L)**	
	With nitrification inhibitor	**Without nitrification inhibitor**	**With nitrification inhibitor**	**Without nitrification inhibitor**
Mixed leachate	4,290	4,346	5,814	5,872
After stripping	3,500	3,330	4,572	4,630
Effluent	*400*	*400*	*400*	*400*

Table B.13 BOD$_5$/BOD$_{20}$ ratio

	BOD$_5$/BOD$_{20}$	
	With nitrification inhibitor	**Without nitrification inhibitor**
Mixed leachate	0.74	0.74
After stripping	0.76	0.72

Table B-14 Variation of MLSS, MLVSS and MLVSS: MLSS ratio

MLSS (mg/L)	**MLVSS (mg/L)**	$\frac{\textbf{MLVSS}}{\textbf{MLSS}}$
16,800	9,450	0.56
29,300	10,300	0.35
5,433	2,817	0.52
3,500	1,580	0.45
2,533	883	0.35
4,467	2,400	0.54
10,917	6,800	0.62
4,817	2,717	0.56
5,720	2,680	0.47
8,525	3,325	0.39
9,220	4,140	0.45
6,500	4,133	0.64
13,860	6,780	0.49
10,140	6,000	0.59
15,275	6,550	0.43
8,220	4,100	0.50
7,283	3,933	0.54
7,960	4,360	0.55
5,283	3,850	0.73
7,733	4,700	0.61
4,517	2,417	0.54
5,200	2,500	0.48
6,420	3,360	0.52
4,733	3,283	0.69
8,250	5,600	0.68
3,120	2,000	0.64
3,917	3,017	0.77
2,560	1,420	0.55
8,900	4,850	0.54
17,100	9,100	0.53
15,267	7,867	0.52
14,067	7,433	0.53
12,567	7,900	0.63
11,560	6,520	0.56
8,125	5,675	0.70
6,167	3,767	0.61
5,580	2,260	0.41
4,500	1,780	0.40
3,583	1,917	0.53
3,100	1,883	0.61
4,750	2,600	0.55

Table B-14 (continued) Variation of MLSS, MLVSS and MLVSS: MLSS ratio

MLSS (mg/L)	**MLVSS (mg/L)**	$\frac{\textbf{MLVSS}}{\textbf{MLSS}}$
6,317	3,583	0.57
7,617	4,350	0.57
4,917	3,000	0.61
5,383	2,617	0.49
5,633	3,667	0.65
6,917	4,033	0.58
8,767	4,867	0.56
8,133	5,017	0.62
8,700	5,100	0.59
10,500	5,917	0.56
12,767	8,183	0.64
13,140	8,560	0.65
22,300	10,060	0.45
15,333	8,367	0.55
23,233	11,867	0.51
17,067	9,967	0.58
14,300	7,533	0.53
13,000	6,467	0.50
15,267	8,200	0.54
9,967	6,533	0.66
11,360	6,800	0.60
6,317	3,583	0.57
7,617	4,350	0.57
4,917	3,000	0.61
5,383	2,617	0.49
5,633	3,667	0.65
6,917	4,033	0.58
8,767	4,867	0.56
8,133	5,017	0.62
8,700	5,100	0.59
10,500	5,917	0.56
12,767	8,183	0.64
13,140	8,560	0.65
22,300	10,060	0.45
15,333	8,367	0.55
23,233	11,867	0.51
17,067	9,967	0.58
14,300	7,533	0.53
13,000	6,467	0.50
15,267	8,200	0.54
9,967	6,533	0.66

APPENDIX D

Results of Molecular weight cut off study

2. Molecular weight cutoff study of ozonated MBR effluent

2.1 Volume balance

Table D-3 Volume balance (Volume in mL)

	Filtered sample	100 kDa retentate	100 kDa permeate	50 kDa retentate	50 kDa permeate	10 kDa retentate	10 kDa permeate	5 kDa retentate	5 kDa permeate
Influent	200	153.6	43.2	0	35.4	0	33.1	0	31.61
Effluent	200	122.2	75.5	0	72.5	0	71.3	29.1	39.2
Ozonated effluent	200	37	161.4	0	158.3	25.2	131.7	95.68	34.07

2.2 COD

Table D-4 COD values in mg/L

	Filtered sample	100 kDa retentate	100 kDa permeate	50 kDa retentate	50 kDa permeate	10 kDa retentate	10 kDa permeate	5 kDa retentate	5 kDa permeate
Influent	2819	2286		0		0		0	1905
Effluent	1943	3542		0		0		2629	1676
Ozonated effluent	1619	3505		0		2514		1562	990

2.3 COD mass balance

Table D-5 COD mass balance in mg/L

	Filtered sample	**100 kDa retentate**	**100 kDa permeate**	**50 kDa retentate**	**50 kDa permeate**	**10 kDa retentate**	**10 kDa permeate**	**5 kDa retentate**	**5 kDa permeate**
Influent	563.8	351.1		0		0.0		0.0	60.2
Effluent	388.6	432.8		0		0.0		76.5	65.7
Ozonated effluent	323.8	129.7		0		63.4		149.5	33.7

2.4 TOC

Table D-6 TOC values in mg/L

	Filtered sample	**100 kDa retentate**	**100 kDa permeate**	**50 kDa retentate**	**50 kDa permeate**	**10 kDa retentate**	**10 kDa permeate**	**5 kDa retentate**	**5 kDa permeate**
Influent	943.7	1018		0		0		0	722.6
Effluent	648	795		0		0		564	460.4
Ozonated effluent	628.5	629.5		0		631		557.4	475

2.5 TOC mass balance

Table D-7 TOC mass balance in mg

	Filtered sample	**100 kDa retentate**	**100 kDa permeate**	**50 kDa retentate**	**50 kDa permeate**	**10 kDa retentate**	**10 kDa permeate**	**5 kDa retentate**	**5 kDa permeate**
Influent	188.8	156.4		0		0		0.0	22.8
Effluent	129.6	97.1		0		0		16.4	18.0
Ozonated effluent	125.7	23.3		0		23.3		53.3	16.2

3. Molecular weight cutoff study of recycled ozonated MBR effluent at 1:1 with ammonia stripped MBR influent

3.1 Volume balance

Table D-8 Volume balance in mL

	Filtered sample	**100 kDa retentate**	**100 kDa permeate**	**50 kDa retentate**	**50 kDa permeate**	**10 kDa retentate**	**10 kDa permeate**	**5 kDa retentate**	**5 kDa permeate**
Influent	200	145.2	51	0	49.3	0	47.7	7.7	40
effluent	200	105.4	93.5	0	91.6	0	89.7	42	46.6

3.2 COD

Table D-9 COD in mg/L

	Filtered sample	**100 kDa retentate**	**100 kDa permeate**	**50 kDa retentate**	**50 kDa permeate**	**10 kDa retentate**	**10 kDa permeate**	**5 kDa retentate**	**5 kDa permeate**
Influent	2083	3293		0		0		2578	1984
effluent	1884	2142		0		0		2062	3888

3.3 COD mass balance

Table D-10 COD mass balance in mg

	Filtered sample	**100 kDa retentate**	**100 kDa permeate**	**50 kDa retentate**	**50 kDa permeate**	**10 kDa retentate**	**10 kDa permeate**	**5 kDa retentate**	**5 kDa permeate**
Influent	416.5	478.1		0		0		19.9	79.4
effluent	376.8	225.8		0		0		86.6	181.2

3.4 TOC

Table D-11 TOC in mg/L

	Filtered sample	**100 kDa retentate**	**100 kDa permeate**	**50 kDa retentate**	**50 kDa permeate**	**10 kDa retentate**	**10 kDa permeate**	**5 kDa retentate**	**5 kDa permeate**
Influent	780	793		0		0		805	596
effluent	494	557		0		0		443.5	358.7

3.5 TOC mass balance

Table D-12 in mg

	Filtered sample	**100 kDa retentate**	**100 kDa permeate**	**50 kDa retentate**	**50 kDa permeate**	**10 kDa retentate**	**10 kDa permeate**	**5 kDa retentate**	**5 kDa permeate**
Influent	156.0	115.1		0		0		6.2	23.8
effluent	98.8	58.7		0		0		18.6	16.7

APPENDIX E

Pictures of the Experiment

Figure E-1 Pathumthani landfill site

Figure E-2 Pathumthani landfill site, leachate

Figure E-3 Pathumthani leachate sampling

Figure E-4 Leachate sampling at Ramindra transfer station

Figure E-5 Membrane bioreactor

Figure E-6 Clean membrane

Figure E-7 MBR in operation

Figure E-8 Foaming in MBR

Figure E-9 Ozonation unit

Figure E-10 Memebrane at the end of the experiment

Figure E-11 Membrane after cleaning with water

Figure E-12 MWCO apparatus (with stirring arrangement)

Figure E-13 MWCO apparatus (without stirring arrangement)

Figure E-14 MWCO experiment

Figure E-15 “Oxitop” BOD apparatus

ADVANCED OXIDATION COMBINED WITH A MEMBRANE BIO-REACTOR FOR LANDFILL LEACHATE TREATMENT

By
Sumitha Sumanaweera

EVA 037078

Examination Committee

Prof: C. Visvanathan (Chairman)

Prof: Shang-Gyoo Shim

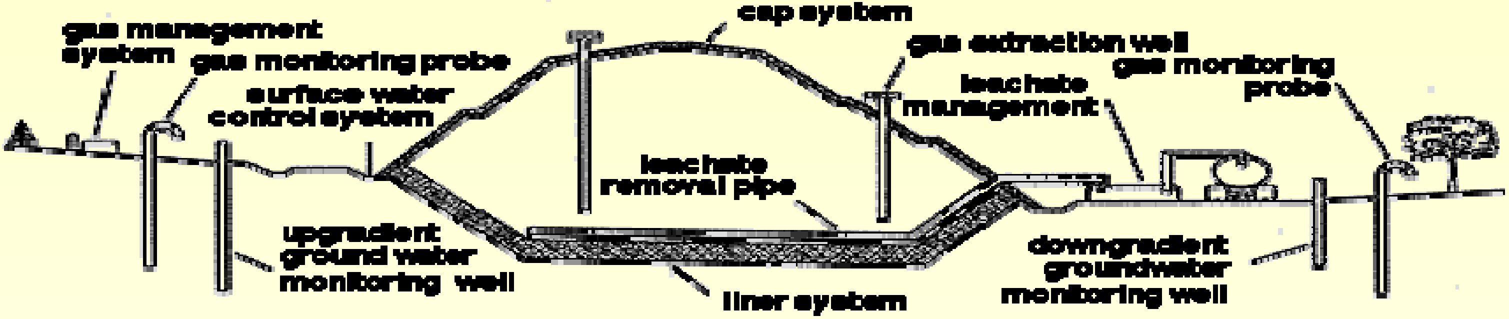
Dr. Thammarat Koottatep

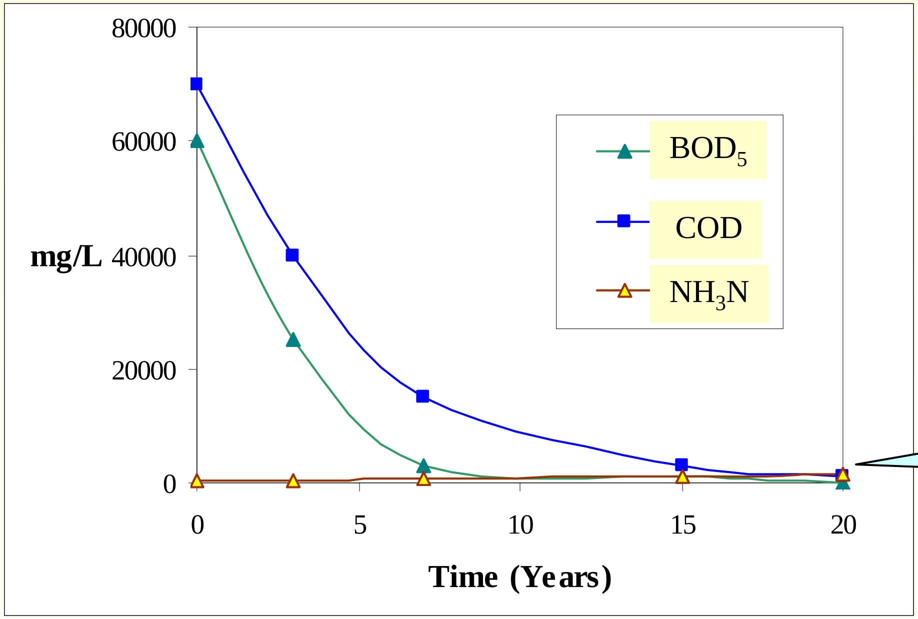
Contents of Presentation

- Introduction
- Literature Review
- Objectives & scopes of study
- Experiment
- Results and discussion
- Conclusions and recommendations

Introduction

Typical schematic of a state-of-the-art landfill





Aerobic → Anaerobic

BOD/ COD 0.8 →0.1

BOD=1,000 mg/L
COD= 3,500 mg/L
NH$_3$N =2000 mg/L

Literature Review

- Leachate Generation composition and Chacterization
  - Lema et al. (1988). Agren, (2003)

- Leachate treatment standards of different countries
  - Hayer and Stegman, (2003). www.cleantechindia.com.

- Biodegradability of leachate at different ages
  - Hayer and Stegmann, (2003). Baig amd Liechti (2001)

- Physico chemical treatment of leachate
  - Ammonia removal, Fletcher and Ashbee (1994)
  - Chemical oxidation, Cossu et al. (2003)
  - Advanced oxidation, Drouche et al. (2003), Shechter (1973)

Literature Review

- MBR
    - Zhou and Smith (2002). Kim and Lee (2003), Chen et al. (2003)
    - Comparison with ASP, Visvanathan et l. (2000)
    - Operation, Yoon et al. (2004)

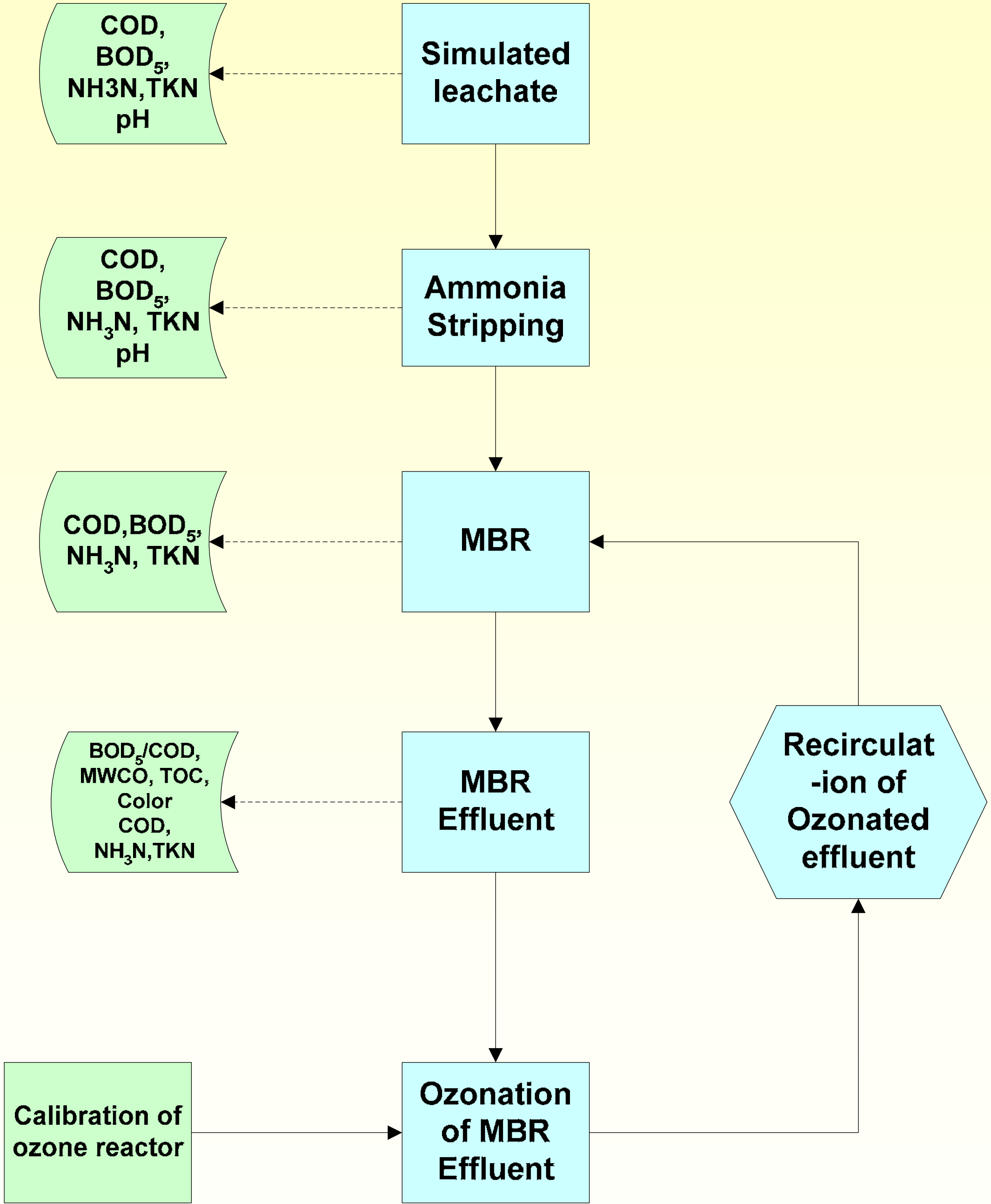
- Activated sludge process
    - Urbain et al. (1998), Thiel (2002), Hanel (1988)
    - Micobiological investigation, Eikelboom (2000)

- Sludge characteristics
    - Jenkins (1993), Sanin (2002), Bura et al. (1996), Liu and Fang (2003)

- Membrane fouling
    - Lee et al. (2002), Mulder (1996)

- MWCO
    - Jimenez et al. (2004). www.millipore.com

Overall experimental plan



COD,
BOD$_5$,
NH3N,TKN
pH

Simulated leachate

COD,
BOD$_5$,
NH$_3$N, TKN
pH

Ammonia Stripping

COD,BOD$_5$,
NH$_3$N, TKN

MBR

BOD$_5$/COD,
MWCO, TOC,
Color
COD,
NH$_3$N,TKN

MBR Effluent

Recirculat-ion of Ozonated effluent

Calibration of ozone reactor

Ozonation of MBR Effluent

Objectives of the study

- **Studying the efficiencies of units of the system**
  - Efficiency of the ammonia stripping process
  - Efficiency of the MBR
  - Efficiency related to Ozonation of MBR effluent
  - Efficiency related to continuous recirculation of ozonated MBR effluent

- **Understanding the refractory nature of leachate by MWCO study**
  - On MBR influent and effluent
  - On ozonated effluent mixed with ammonia stripped leachate as MBR influent and the corresponding effluent

Scopes of the study


Ramindra

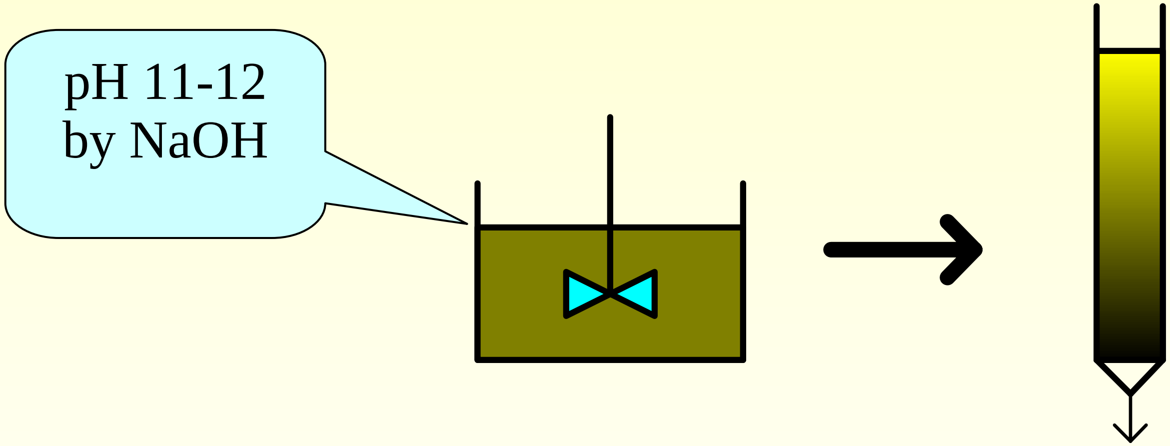

Pathumthani leachate


Pathumthani lagoon

- Medium age leachate was used by mixing young and old leachate
- Ozonation was done in a batch study and then proceeded with a continuous study

Methodology : Ammonia stripping

$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3$$

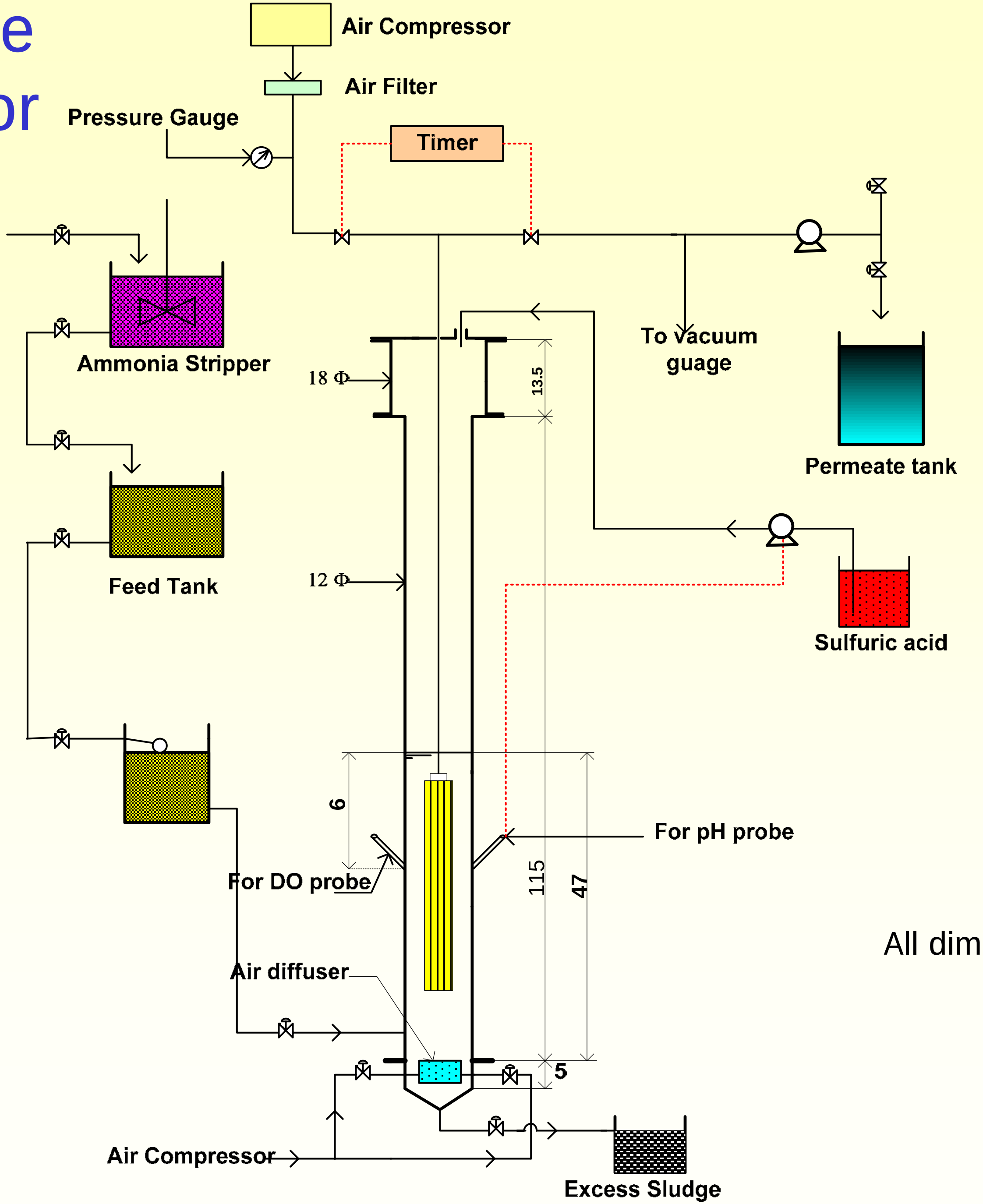


pH 11-12
by NaOH

5 hr stripping

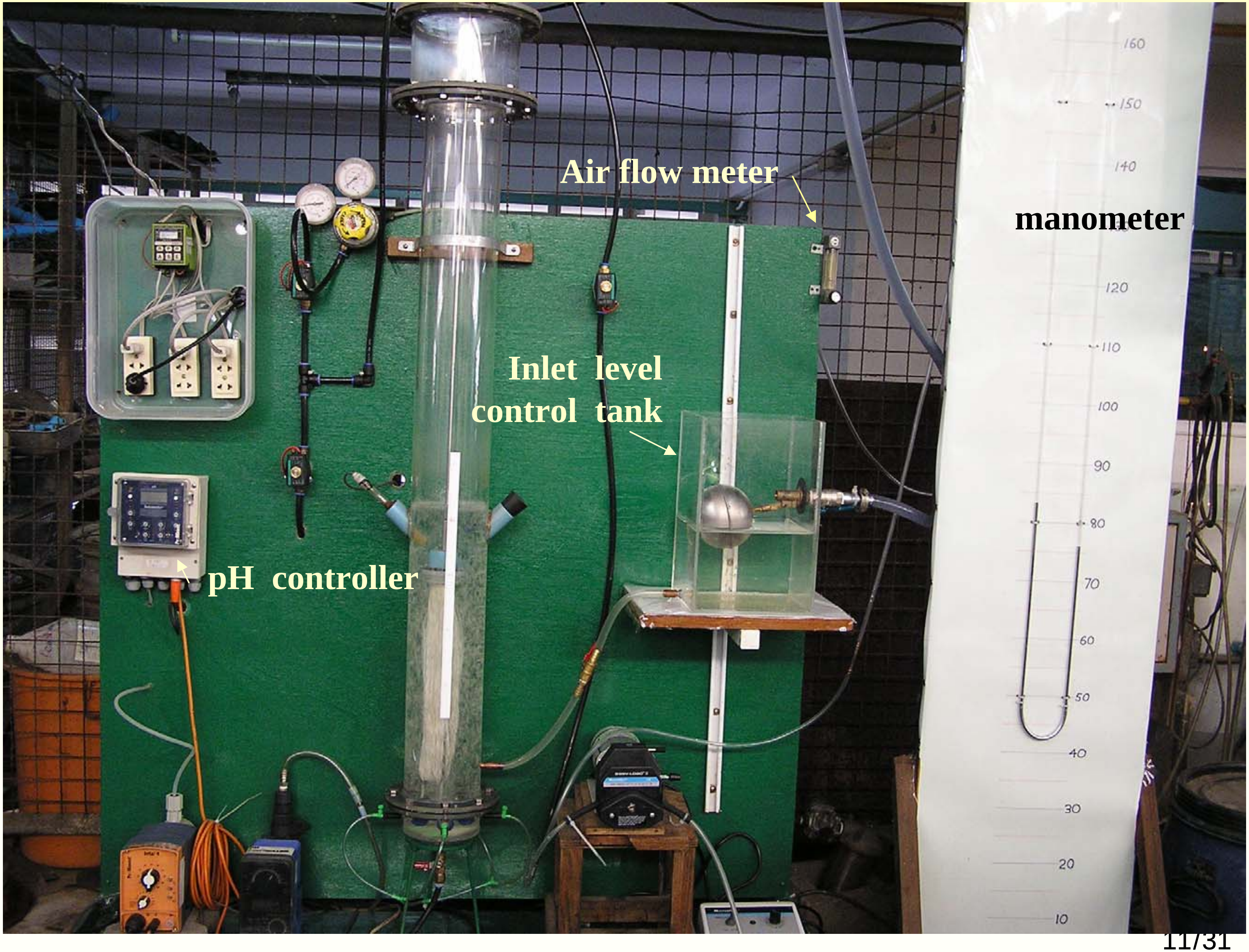
3 hr settling

Membrane Bio-reactor

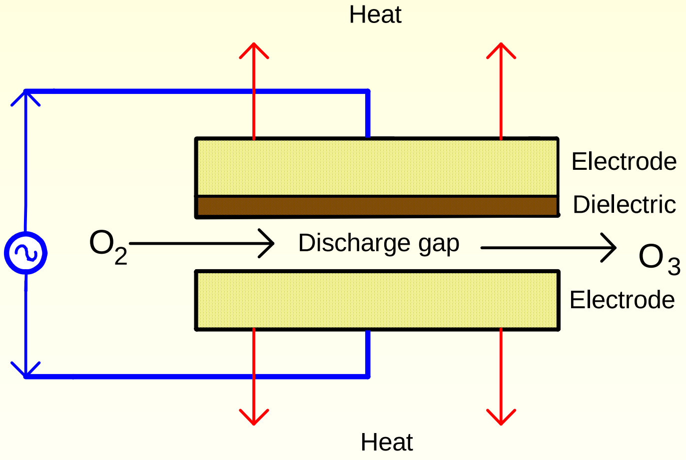


All dimensions are in cm

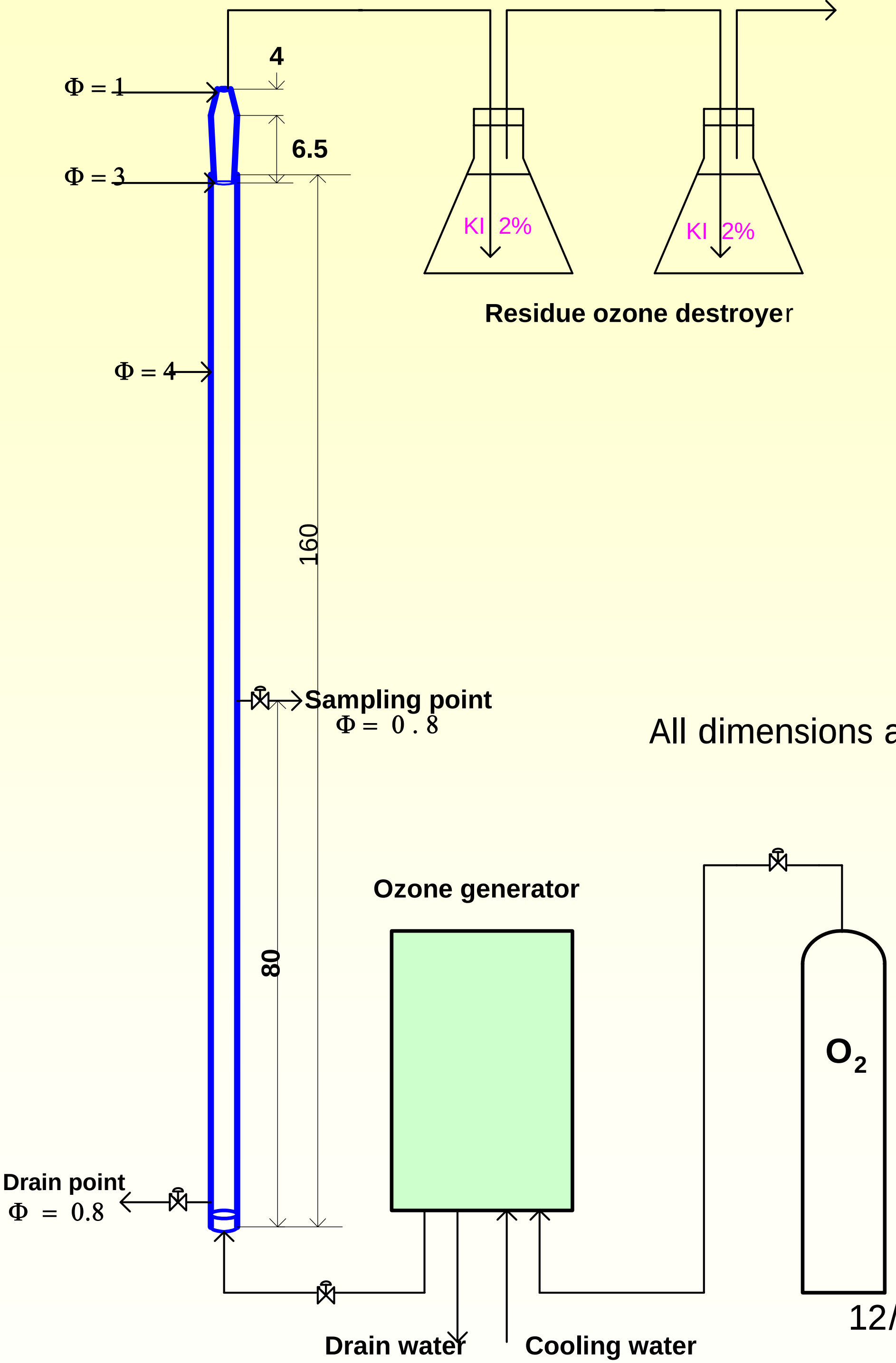
Membrane bio-reactor



Ozonation system

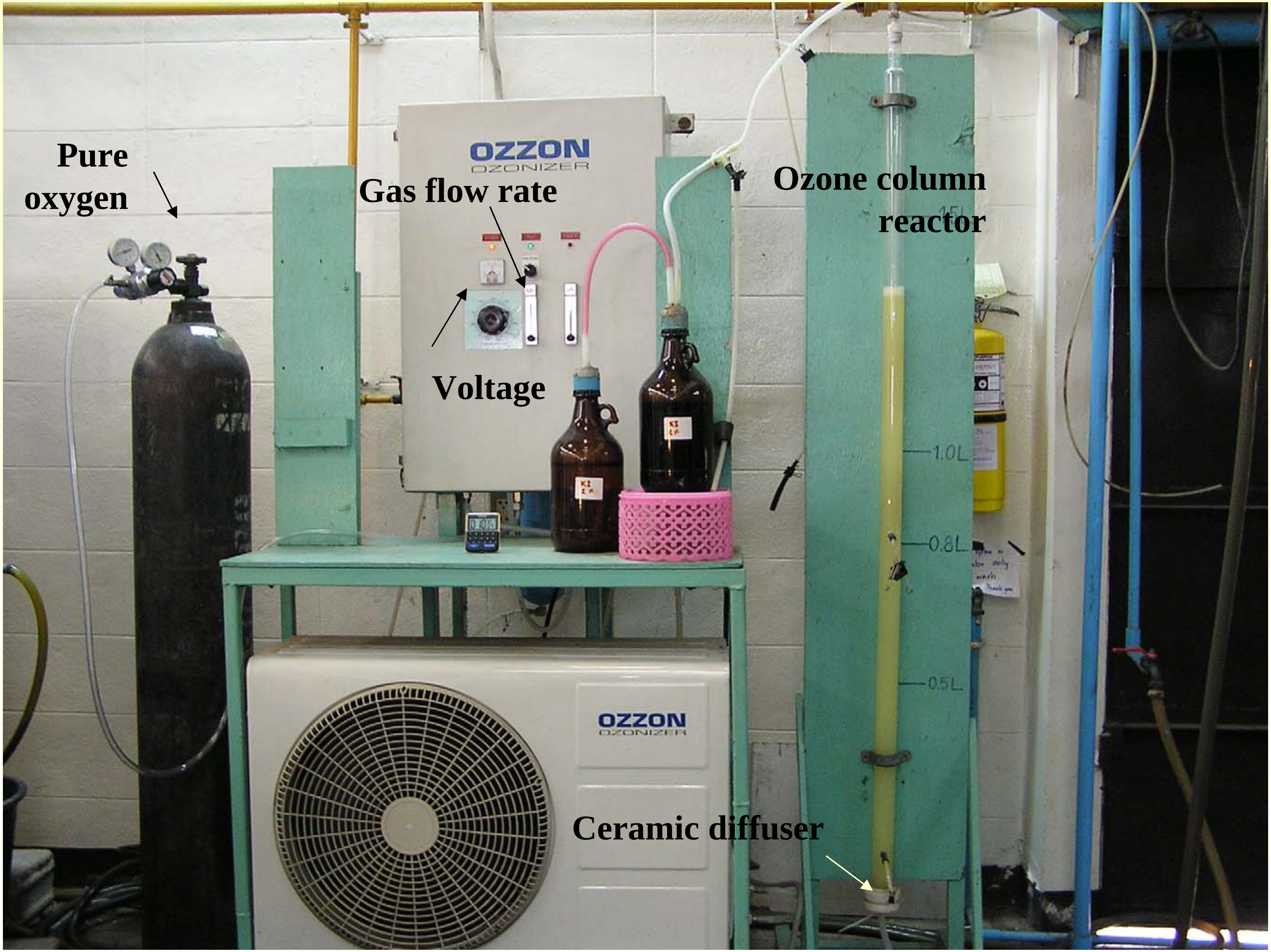


Corona discharge method



All dimensions are in cm

Ozonator

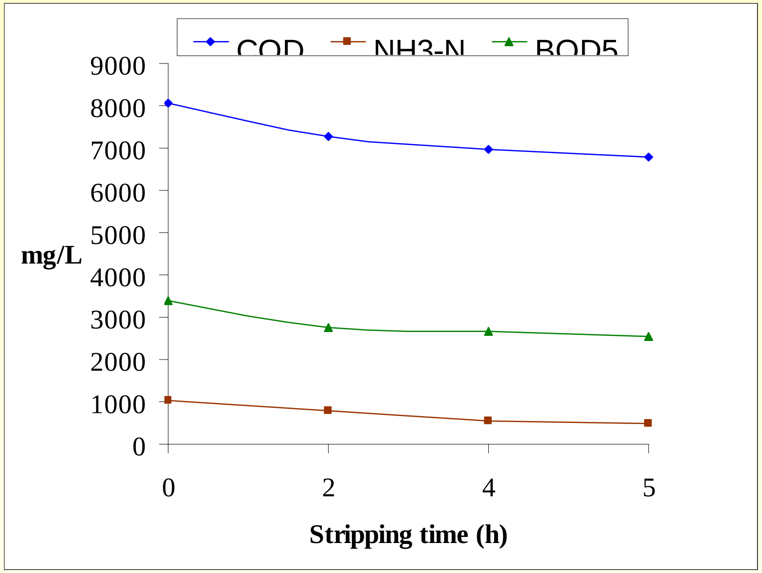

Pure oxygen
Gas flow rate
Voltage
Ozone column reactor
Ceramic diffuser
OZZON OZONIZER
1.0L
0.8L
0.5L
OZZON OZONIZER

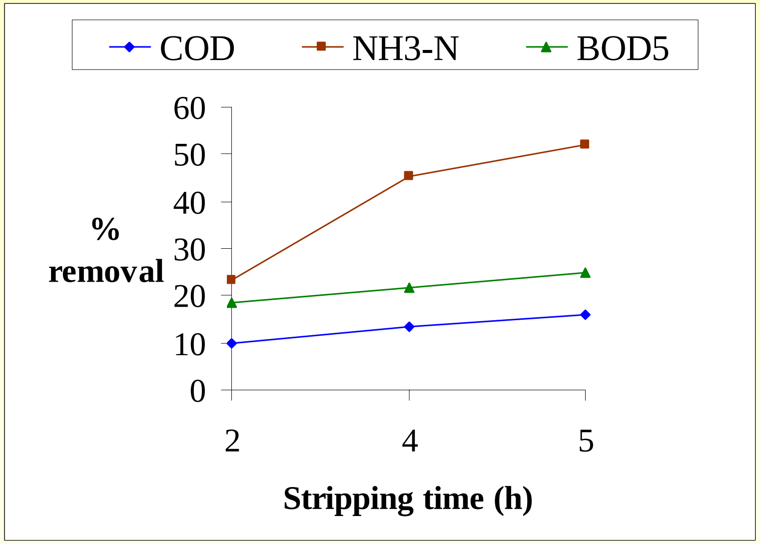
MWCO study

Stirring module

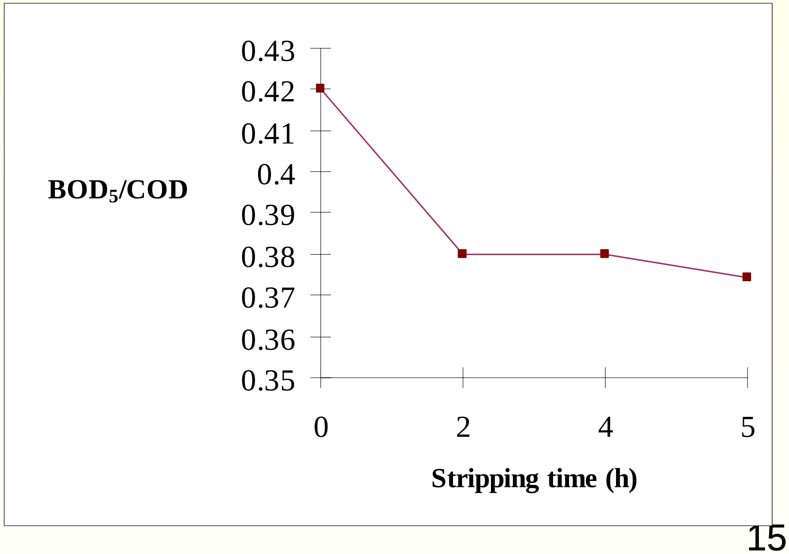
Non stirring module

Results of the ammonia stripping experiment

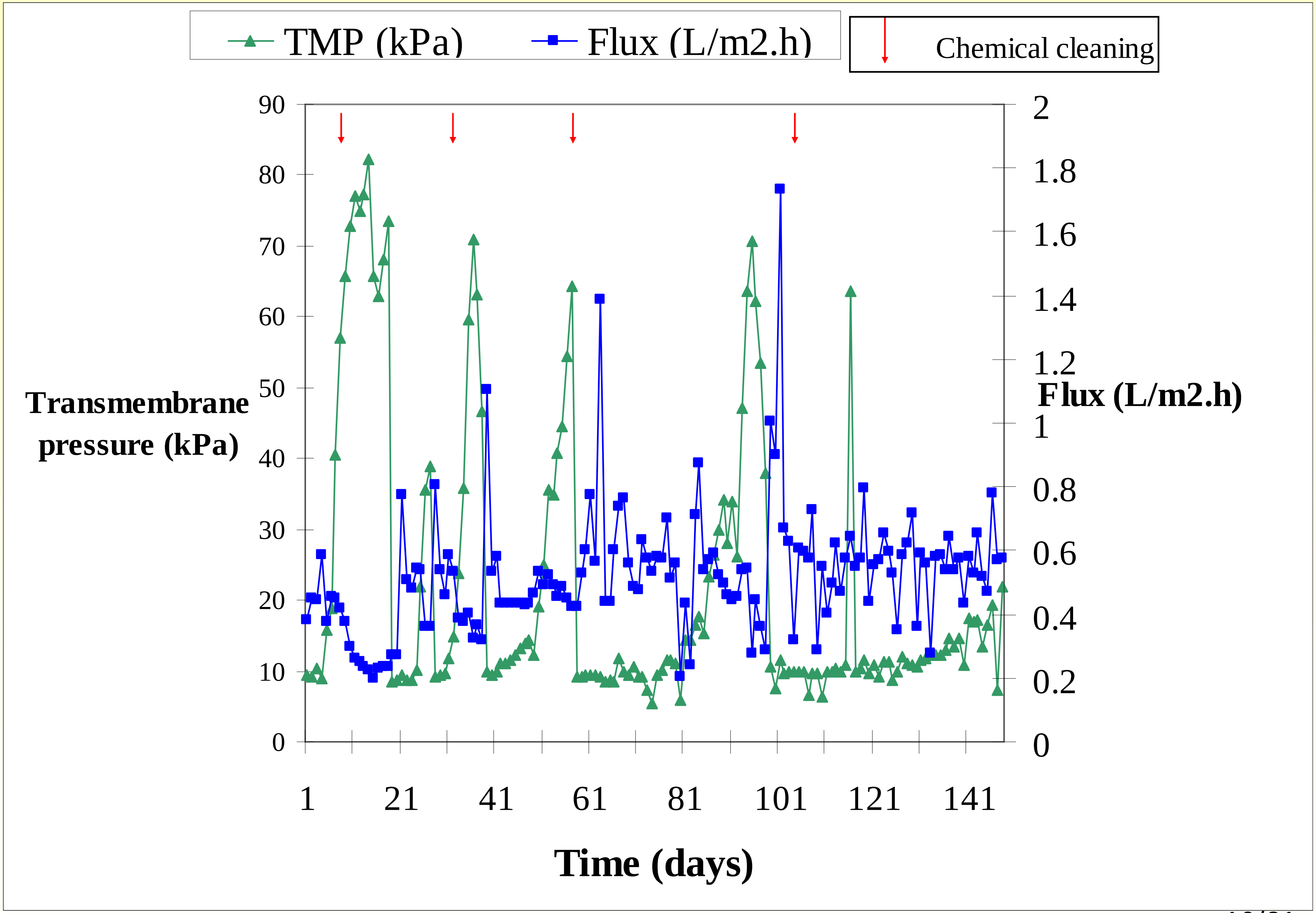




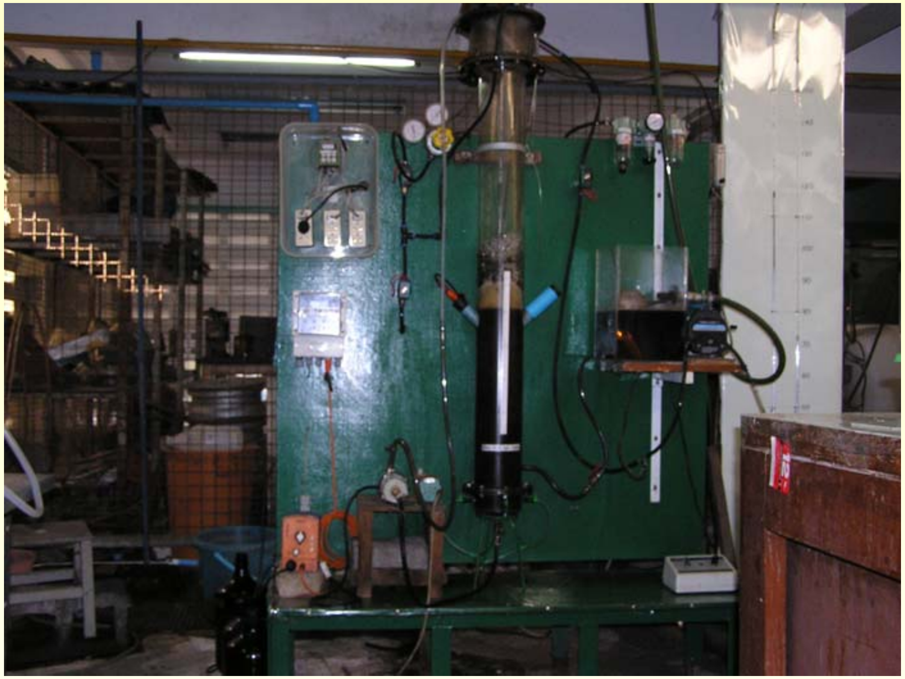
- Ammonia stripping efficiency 59%
- Stripping time established to 5 hr.
- BOD_5/COD dropped from 0.42 to 0.37
- COD dropped 36%
- BOD_5 reduced about 25%



MBR operation



MBR in operation



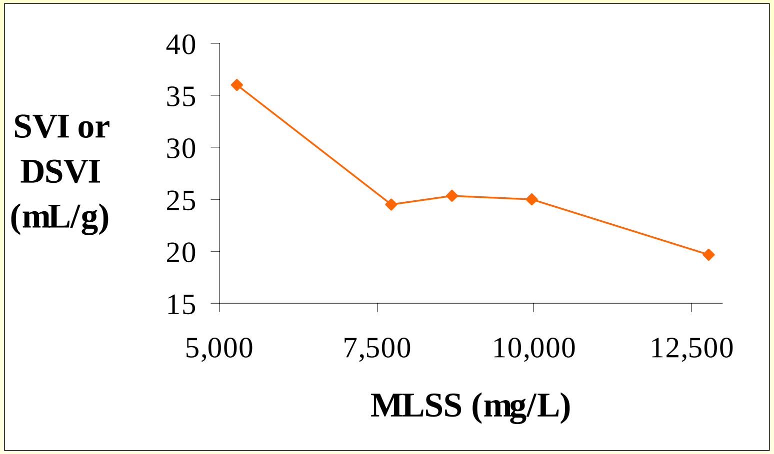
Foaming in MBR

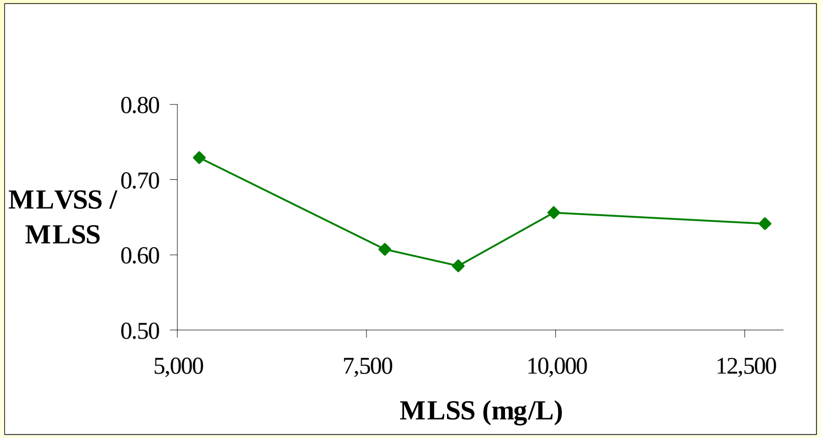
MBR Efficiency

- COD removal 72%
- BOD_5 removal 93%
- TKN removal 36%

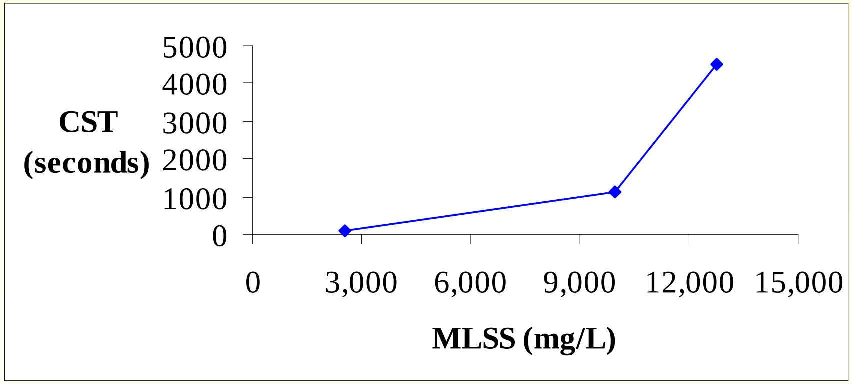
- Membrane fouling rate reduced with the increase of MLSS

MBR Sludge Analysis





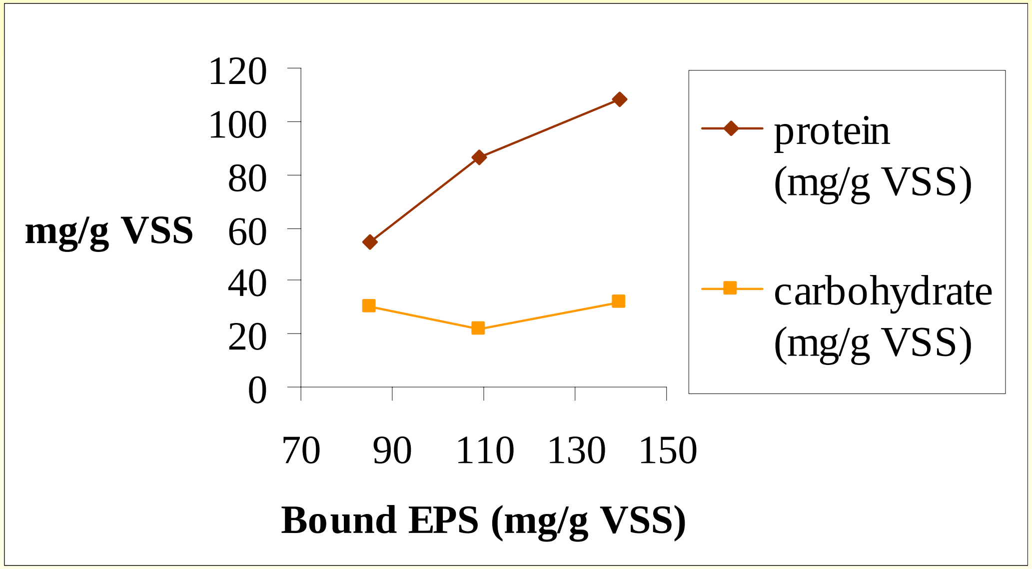
- Average MLVSS/MLSS ratio was 0.55

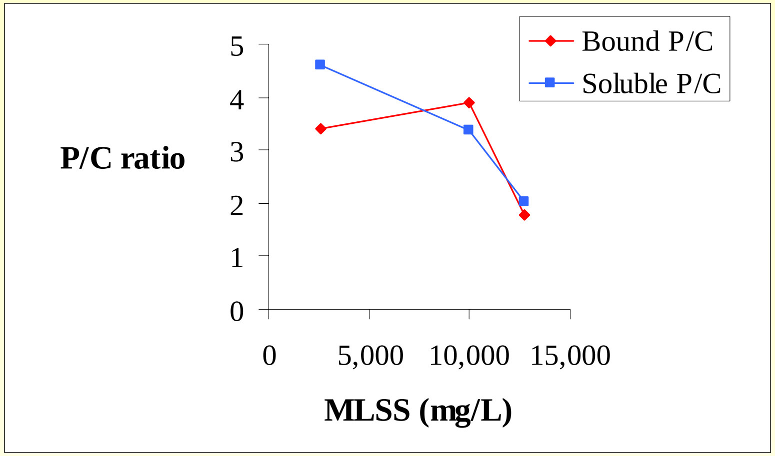


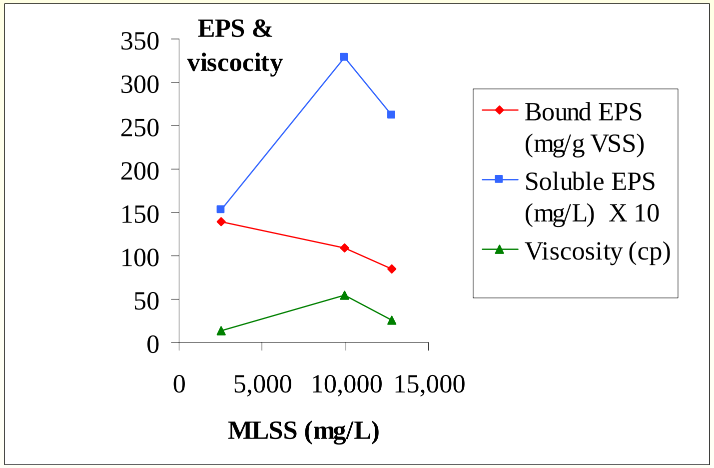
- DSVI was 25 mL/g at MLSS 10,000 mg/L Increase of MLSS made sludge difficult to settle

- Sludge dewaterability in terms of CST increased with MLSS

MBR Sludge Analysis







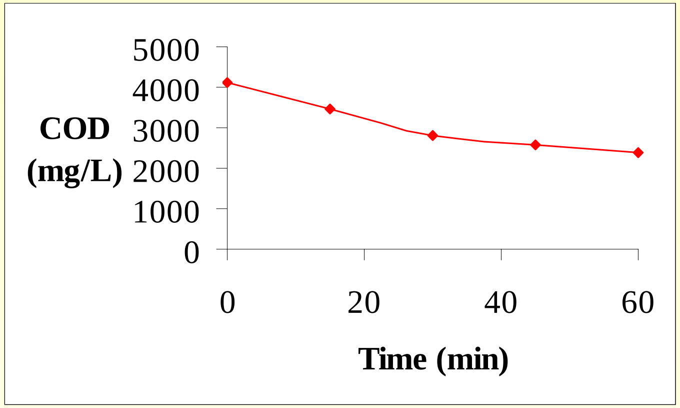
- Reduction of bound and soluble protein to carbohydrate (P/C) ratio indicates the difficult to settle character of MBR sludge

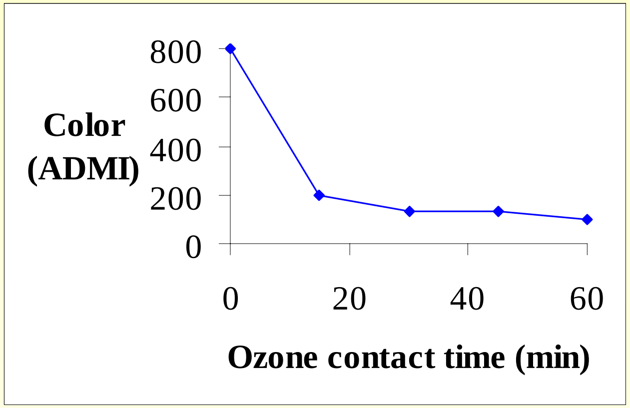
Membrane of MBR

Membrane immediately after the test period

Membrane after cleaning with water

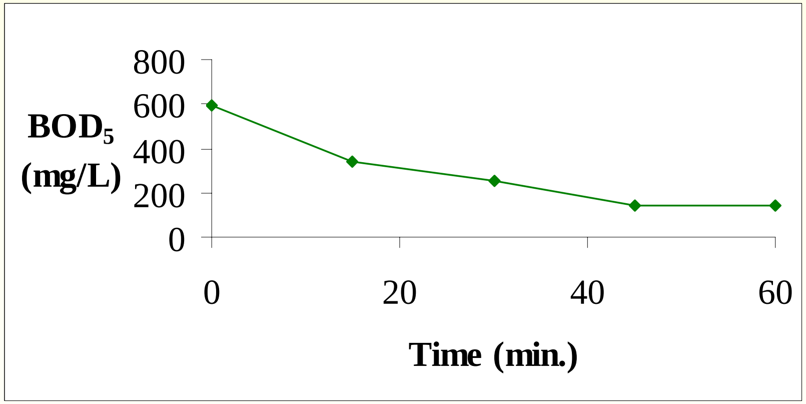
Ozonation of MBR effluent

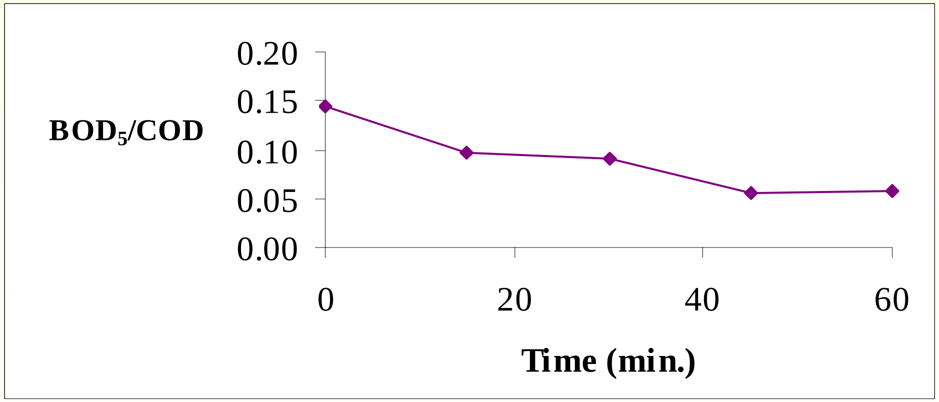




Ozone contact time - 30 minutes

Color removal - 83%

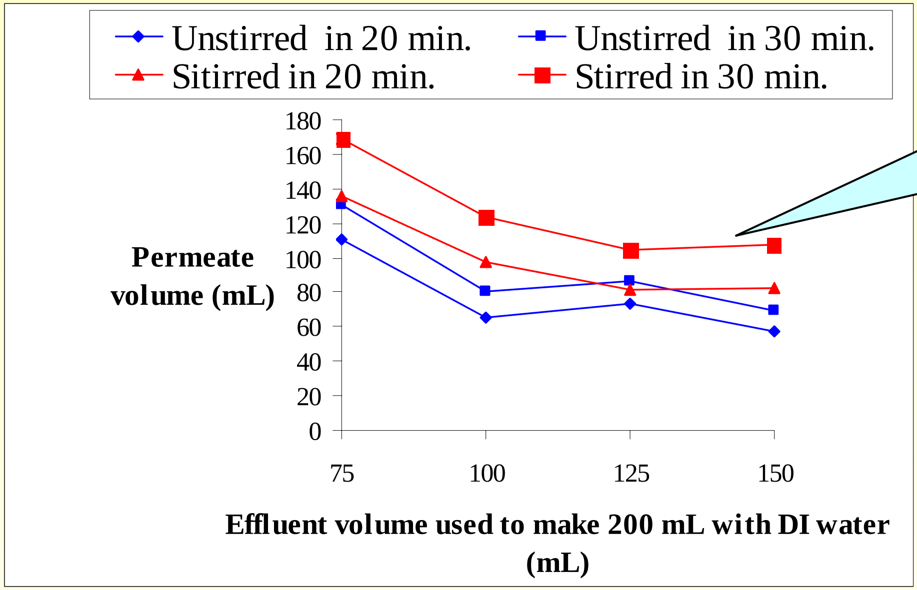




BOD$_5$ removal - 57%

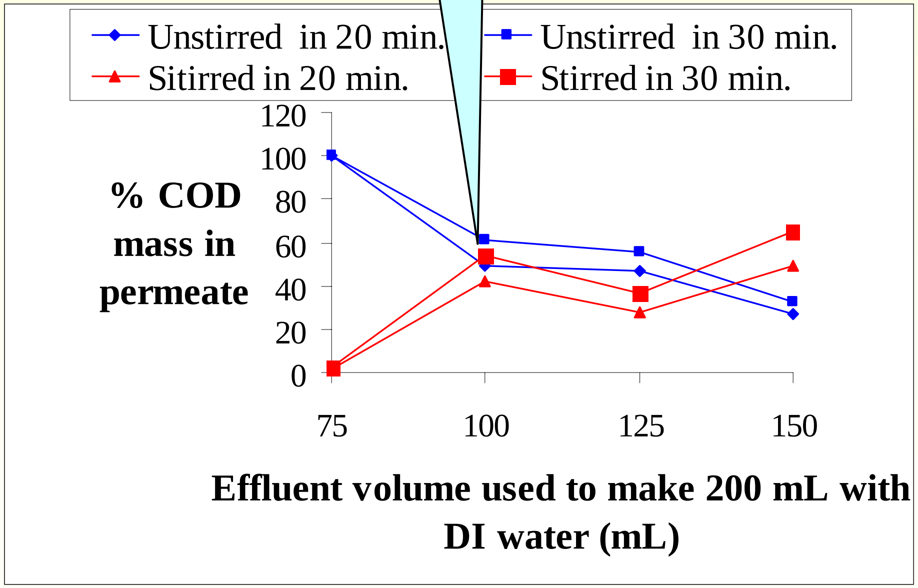
BOD$_5$/COD ratio drop - 0.14 to 0.09

Standardization of MWCO experiment



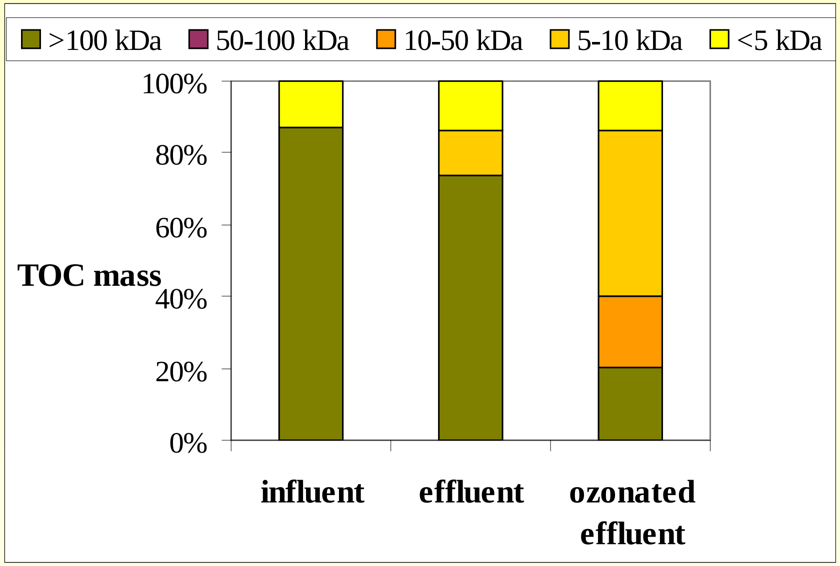
More filtrate in stirred case

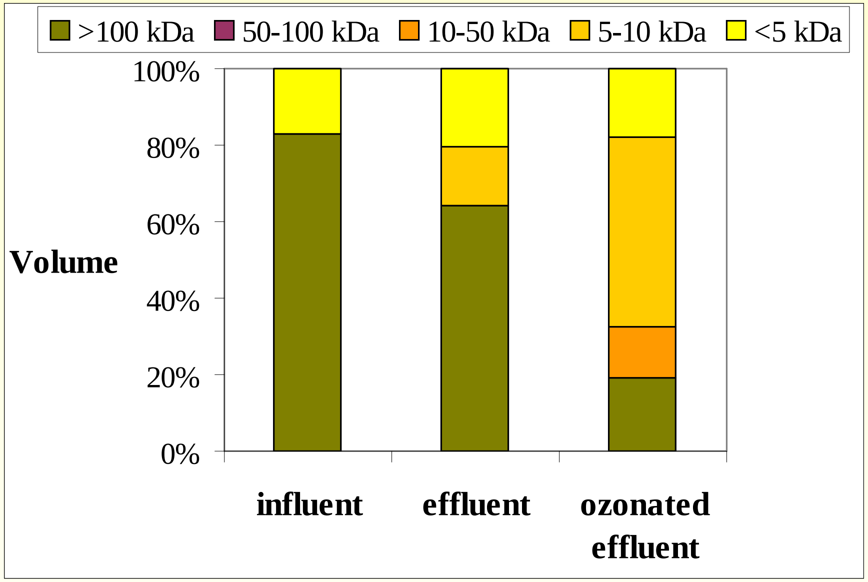
COD passed coincide

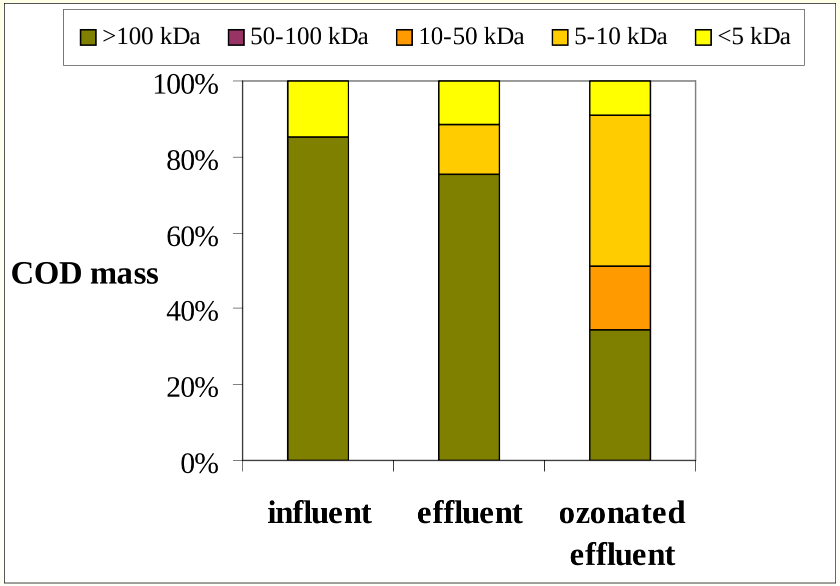


- MWCO was standardized to 1:1 dilution, 200 mL volume, 2 bar N_2 pressure and 30 minutes stirred filtration

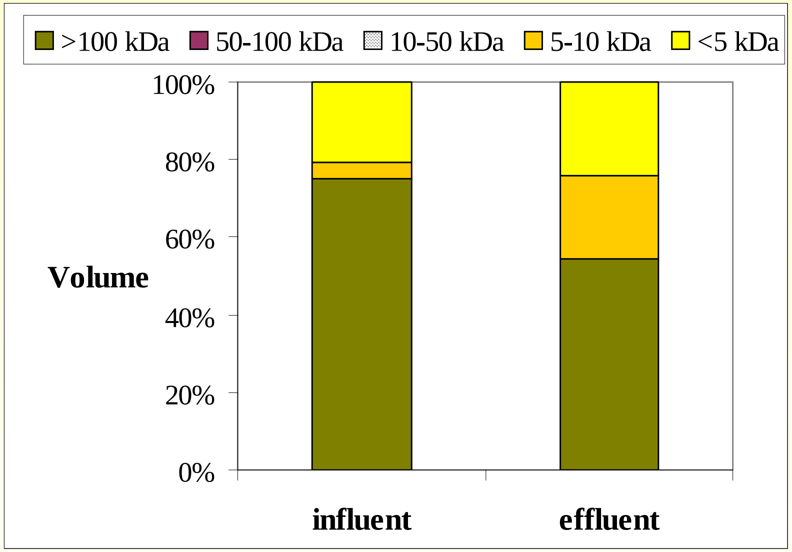
MWCO of ozonated MBR effluent

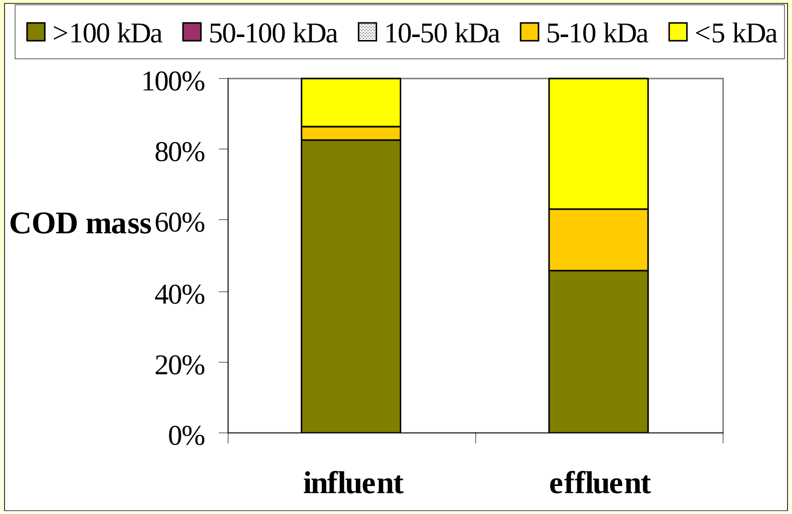


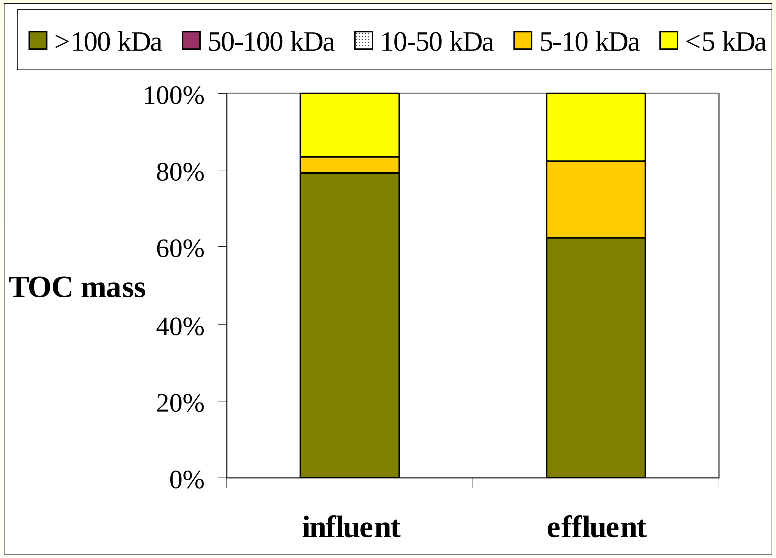




MWCO after recirculation of ozonated MBR effluent







MBR efficiency before and after ozonated effluent recycle

	MBR efficiency %			BOD / COD	
	COD	**TOC**	**BOD**	**Influent**	**Effluent**
Before ozonation	31	31	93	0.22	0.02
After ozonation	46	37	83	0.18	0.09

Conclusions

1. Ammonia stripping process was 59% efficient. COD reduction was 36%. BOD_5/COD dropped from 0.42 to 0.37

2. MBR COD removal efficiency was 71.5%. BOD_5 removal efficiency was 93%. TKN removal efficiency was 36%

3. Average MLVSS/MLSS of MBR was 0.55. Sludge is difficult to settle. Drop in protein : carbohydrate ratio with increasing MLSS shows difficulty in settling.

4. Sludge is difficult to dewater as CST increased with the increase of MLSS.

5. Ozone contact time required to reduce COD and color of the effluent to constant value was 30 minutes. Ozonation caused 32% COD reduction and 57% BOD_5 reduction. BOD_5/COD dropped from 0.14 to 0.09.

Conclusions

6. Ozonation removed 83% of color in MBR effluent

7. MWCO study was standardized to initial volume of 200 mL of 1:1 dilution with DI water with nitrogen pressure of 2 bar for 30 minutes.

8. MWCO revealed that MBR effluent had about 20% refractory volume fraction. It was observed that the biological process has created a 5-10 kDa molecular fraction which increased three folds during ozonation. A new 5-10 kDa fraction was generated upon ozonation.

9. Continuous recirculation of ozonated MBR effluent in 1:1 ratio did not show the 10-50 kDa molecular fraction in ozonated effluent

10. Continuous ozonated effluent recycle improved COD removal efficiency from 31% to 46%. TOC removal also improved from 31% to 37%. BOD_5 removal dropped from 93% to 83%.

Therefore the improvement of efficiency is low in magnitude.

Recommendations

1. Low BOD_5/COD ratio of 0.27 - 0.37 range and low MLVSS/MLSS ratio of 0.55 in MBR suggests the presence of refractory organics in the sludge. As a means of better sludge disposal, sludge ozonation and recirculation study is recommended.

2. Oxygen uptake rate study is recommended to compare MBR sludge with conventional activated sludge.

3. As molecular weight of protein can vary according to the changes of ionic strength of solution and pH, further studies on MWCO based on pH variations are recommended.

4. Study to identify predominant compounds found in each molecular weight fraction of MWCO study could lead to better understanding of possibilities for further treatment of effluent.

Recommendations

5. The continuous recirculation of ozonated effluent test could be performed only for 3 days due to limitations of time. Prolonged duration of test with precisely monitored ammonia stripping is recommended.

Thank You