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Oxygen transfer and transport resistance across silicone tubular membranes

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Abstract

Dissolved oxygen is used as an electron acceptor in aerobic organic waste digestion in biological processes. To enhance production of intermediate metabolic products such as acetate in anaerobic conversion, small amounts of oxygen is needed. The process is then called combined microaerobic and anaerobic. One strategy of supplying oxygen is to dissolve it in water and transfer it across a dense polymeric membrane to the biological medium. Thus experimental data on oxygen flux and flow resistance are needed. In this study, an experimental method is proposed to determine the transport rates and total resistance of flow across silicone tubular membranes by using bulk oxygen concentration measurements. The biological medium inside the reactor is replaced by a known volume of distilled water. Dissolved oxygen is removed from the distilled water by purging nitrogen gas. Water to be circulated inside the membrane is saturated with oxygen by purging either with pure oxygen or air. This oxygen saturated water is supplied to the reactor by flushing inside the silicone tube. Experiments with different temperatures inside and outside the tubular membranes are also performed. Variations of bulk oxygen concentrations with time inside the reactor are measured using calibrated microelectrodes. At room temperature, both thin and thick membranes produced the lowest oxygen transfer rate when water saturated with air was supplied inside the membranes. The highest oxygen transfer rates were reported when pure air (not dissolved in water) was supplied inside the membrane. When the reactor was held at 55^0C, both membranes showed a reduction of oxygen transfer rates compared to the room temperature experiments. Results obtained can be used as a tool to screen different membrane design options and estimate oxygen supply rates in membrane integrated biological processes.

Key words: Dense tubular membranes; Dissolved oxygen; Biological processes; Microaerobic; Flow resistance

1. Introduction

Applications of membranes have been found in a variety of purposes in waste management such as **separation of solids**, **biomass retention**, **and aeration of bio reactors** and **extraction of pollutants** from waste water [7]. Gas permeable membrane which transfers components from gas phase to liquid phase is arranged in a reactor vessel so that liquid and gas compartments are formed. Unlike in conventional technologies, liquid and gas flow can be varied independently without problems of flooding, foaming etc. When there is high oxygen demand for waste digestion particularly in aerobic digestion, it can be transferred via gas permeable membrane with high transfer efficiency. By doing so low solubility of oxygen in water and stagnant boundary layer resistance can be overcome. This oxygen diffusion through dense gas permeable membrane can be achieved with high oxygen pressures. By regulating this pressure, oxygen penetration depth into bio film can easily be controlled. When process dictates minor amount of oxygen supply under microaerobic condition, it can also be achieved using dense membranes

The membrane usually acts as support media for biofilm development at the membrane liquid interface. Due to high mixing conventional processes prevent formation of biofilms. Instead oxygen can be supplied via membrane without any bubble formation promoting biofilm activities. Plate and frame, tubular and hollow fibre membrane configurations have been used in membrane aeration processes. But work using dense polymers has largely focused on tubular silicone membranes due to their high oxygen permeability and high chemical and mechanical resistance. Therefore it is needed to develop new strategies to supply oxygen through tubular membranes in waste digestion

2. Theory

The transport of gases through a dense polymeric membrane is generally due to solubility and diffusion. This overall mechanism is known as **permeation**. The important feature of dense membrane is its ability to control the permeation of different components [4]. The transport of oxygen molecule through membrane is described as follows. Starting from bulk phase which is water inside membrane, oxygen molecule transport across diffusion barrier and dissolve in the membrane due to adsorption or absorption. Then it diffuses through the membrane and desorption occurs at the other side and move across the diffusion barrier again and into the bulk of liquid which is inside of reactor (Fig.1) This solution diffusion mechanism is driven by the difference in the thermodynamic activities existing at the up and down stream faces of the membrane and also due to interaction between permeate molecules and membrane material. The solution-diffusion model assumes that the pressure within membrane as uniform and the chemical potential gradient across the membrane is expressed as concentration gradient.

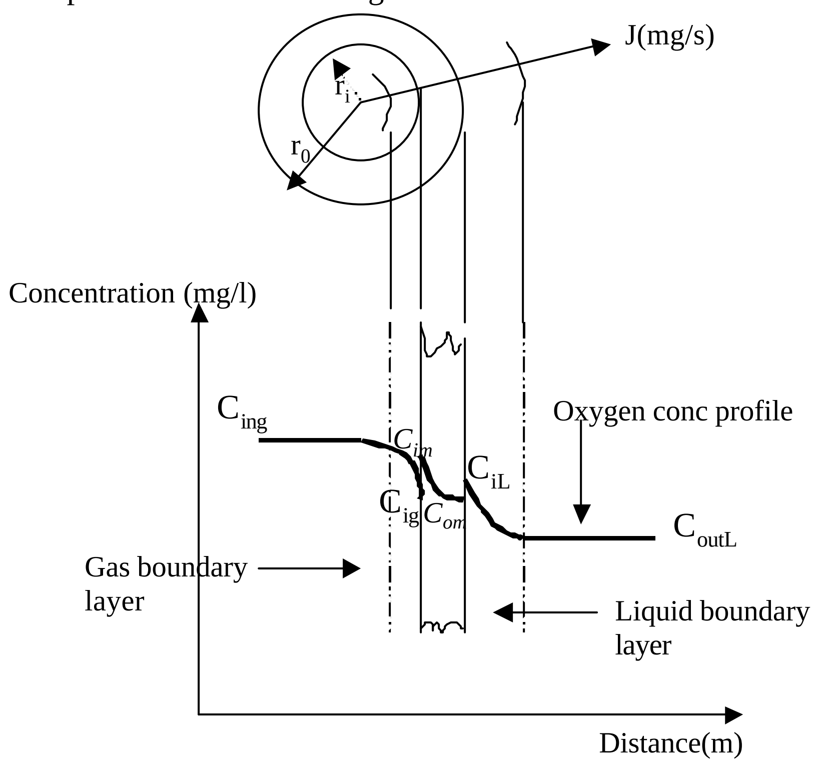


Fig.1. Transport of oxygen through tubular membrane.

At any time t

Transport rate of oxygen across gas boundary layer is given by

$$J_i = k_g .2p.r_i L\left(C_{ing} - C_{ig}\right) \quad \left(\frac{mg}{\min}\right) \tag{1}$$

Inside membrane

$$J_i = -D\frac{dc}{dx} = D.2p.L\frac{\left(C_{im} - C_{om}\right)}{\ln\frac{r_0}{r_i}} = \frac{D.S}{\ln\frac{r_0}{r_i}}\left(C_{ig} - C_{iL}\right) \quad \left(\frac{mg}{\min}\right) \tag{2}$$

Transfer rate across liquid boundary layer

$$J_i = k_L.2.p.r_0 L(C_{iL} - C_{outL}) \quad \left(\frac{mg}{\min}\right) \tag{3}$$

By combining equation 1, 2 and 3 and based on the outside surface area of the membrane

$$J_i = \frac{(C_{ing} - C_{outL})}{\left(\frac{1}{k_g.2.p.r_i L} + \frac{\ln\frac{r_0}{r_i}}{D.S.2.p.L} + \frac{1}{k_L.2.p.r_0.L}\right)2p.r_0 L} \quad \left(\frac{mg}{m^2.\min}\right) \tag{4}$$

Therefore Overall resistance R based on out side surface area of membrane is given by

$$R = \frac{r_0}{r_i.k_g} + r_{0.}\frac{\ln\frac{r_0}{r_i}}{D.S} + \frac{1}{k_L} \quad \left(\frac{\min}{m}\right) \tag{5}$$

Where

C_{ing} - Bulk oxygen concentration inside membrane (mg/l)
C_{ig}- oxygen concentration at gas membrane interface
C_{im}- oxygen concentration inside membrane at gas side
C_{om}- oxygen concentration inside membrane at liquid side
C_{iL}- oxygen concentration at liquid membrane interface
k_g - Gas side individual mass transfer coefficient (m/s)
k_L- Liquid side individual mass transfer coefficient
r_0 -Outside radius of tubular membrane
r_i - Inside radius of tubular membrane
L = length of the membrane (m)
D - Diffusion coefficient inside membrane
S - Solubility coefficient inside membrane
Permeability coefficient is defined as P = D.S

Note:

Total resistance R is experimentally determined in this investigation Temperature effect on both diffusivity and permeability in dense polymer membrane can be represented in the form of empirical Arrhenius relations. These imply the increase of diffusivity and permeability with increase in temperature.

Diffusivity is given by

$$D = D_0 \exp(-E_d/RT) \tag{6}$$

Permeability is given by

$$P = P_0 \exp(-E_p/RT) \tag{7}$$

Where D_0 and P_0 are pre exponential factors, E_d and E_p are apparent activation energies, R is universal gas constant and T is absolute temperature.

3. Material and methods

3.1 Materials

3.1.1. Silicone tubular membranes

Two types of tubular membrane with varying thickness were used in this investigation

a. Thick membrane : Length 5.34m , External diameter 4mm, Surface area: 0.0671 m^2
b. Thin membrane : Length 2.75m, External diameter 3mm, Surface area : 0.02592 m^2

3.1.2. Membrane bioreactor

Reactor vessel as shown in Fig.2 was filled with distilled water and tubular membrane winded metal support was immersed in water. Volume of water used is given as below

a. For thick membrane Experiments

All room temperature Experiments: Volume of water inside reactor = 2516 ml

All elevated temperature Experiments: Volume of water inside reactor = 2516 ml

(See Experiments for thick membrane given under Table. 1,page 7)

b. For thin membrane experiments

Room temperature Experiments i.e. both oxygen dissolved water and membrane bioreactor are at room temperature

Volume of water in side reactor = 1570 ml

Oxygen dissolved water at room temperature and reactor at 55°C

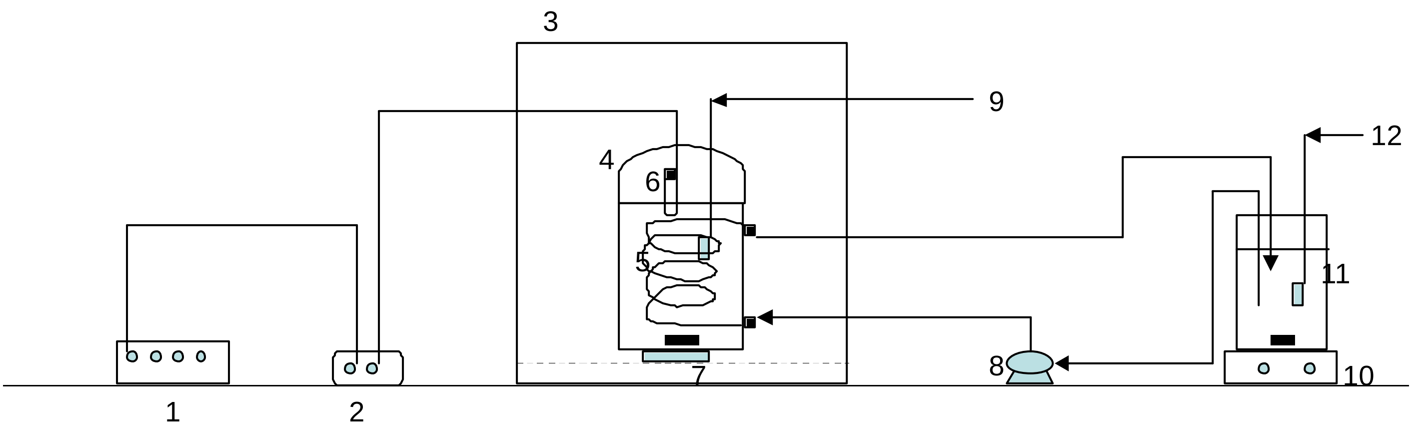
Volume of water inside reactor = 1440 ml

Microelectrodes: LAZER Research Laboratories, Inc. Model DO-166FT flow through dissolved oxygen probe and potentiometer

Transmitter for pH and Redox**:** Mycom CPM 152 Transmeter for pH and Redox. Maximum scale is 2000mV

Peristaltic pump, Magnetic stirrers, Nitrogen/Oxygen/Air supplies, Autoclave, Distilled water, Thermometer

To conduct experiments above mentioned materials are arranged as shown in Fig.2.



1. Transmeter for pH and Redox
2. Dissolved oxygen probe
3. Autoclave
4. Reactor
5. Silicone Tubular membrane
6. Micro electrode
7. Magnetic stirrer
8. Pump
9. N_2 supply
10. Magnetic stirrer
11. Water beaker
12. Air/ pure oxygen supply

Fig.2. Schematic diagram of Experimental set-up

3.2. Electrode assembly and calibration

3.2.1. Electrode assembly

By holding electrode with tip facing up and cable facing down, electrode mouth was filled with filling solution until it reaches top of the electrode (see Fig.3) by ensuring filling of middle chamber. After placing membrane on the top of the electrode, O-ring was forced into groove of electrode body making a proper seal between electrode and membrane.

3.2.2. Electrode calibration

At the beginning, out put cable from electrode was connected to transmeter. In this Exp. Oxygen is dissolved into distilled water by means of air purging and pure oxygen purging. Air was purged into distilled water containing beaker while it was being mixed with magnetic stirrer. Electrode was partially immersed into water and power on combining with potentiometer. After sometime, transmeter mV reading was stable around fixed value. At this time, using mini screw driver, cal potentiometer was adjusted to a new mV reading which was the calibrated value for known oxygen concentration in the water.

3.2.3. Zero calibration

By purging nitrogen gas into water inside the reactor vessel which is air tight, started removing dissolved oxygen while it is being thoroughly mixed. Electrode was partially immersed in water inside reactor and it could be noted that decrease in mV reading. When all the oxygen removed, reading was stable around zero mV. At this time Zero potentiometer was adjusted to 0 mV reading.

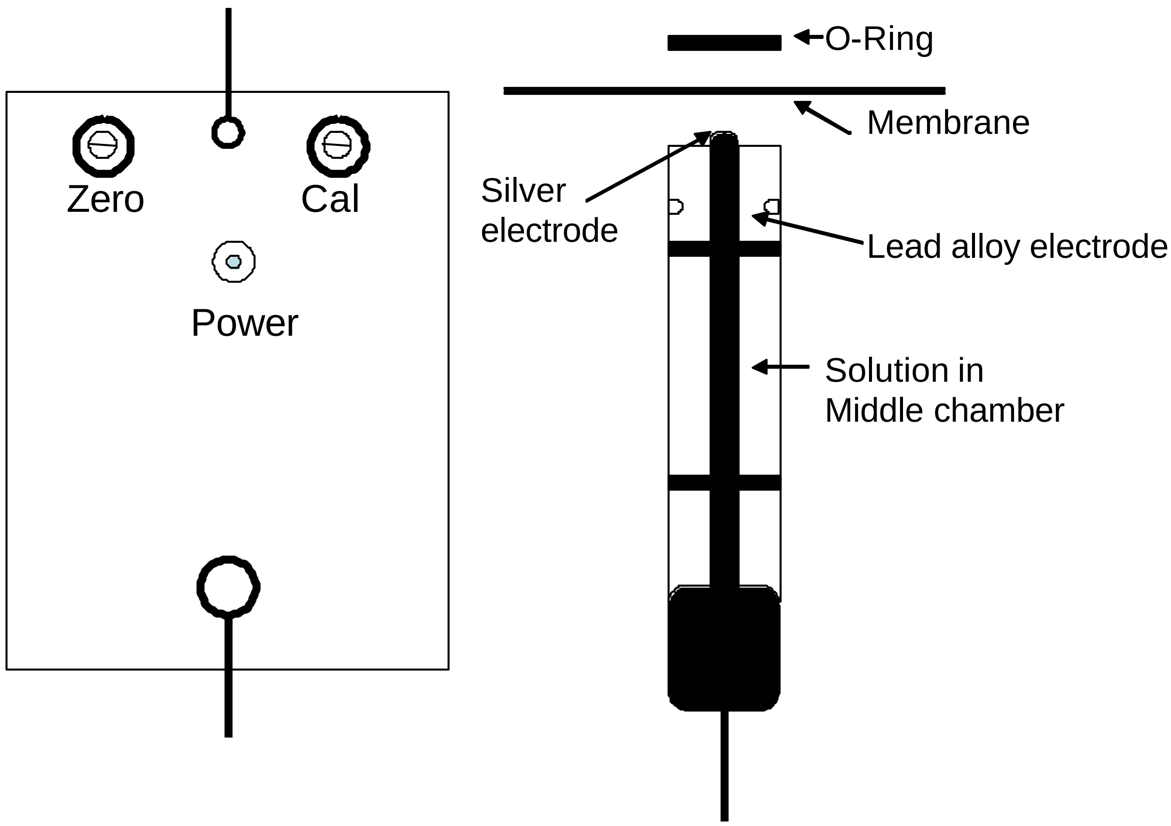


Fig.3. Assembly of microelectrodes

4. Experiments using thick tubular membrane

4.1. Designation of Experiments under different operating conditions

Different experiments were conducted by varying oxygen supplying method and temperature conditions at which membrane bioreactor and oxygen dissolved water are held (Table 1)

Table.1. Definitions of Experiments for thick membrane

	Thick membrane		
Experiment	Temperature (°C)		
	Membrane bioreactor	**Oxygen dissolved water**	**Oxygen supply method**
Exp.1TH	21	21	Air purging
Exp.2TH	21	21	Oxygen purging
Exp.3TH	55	40	Oxygen purging
Exp.4TH	55	21	Oxygen purging
Exp.5TH	55	19	Air purging

4.2. Results and discussion under different Experiments

4.2.1. Exp. 1TH

Oxygen is dissolved in water by means of *air purging.* Both oxygen dissolved water and membrane bioreactor are kept at room temperature (21°C).

As explained above, calibration was done for air purging. While air was being purged into water, mixing was accomplished by a magnetic stirrer. By partially immersing the tip of the electrode in water, transmeter mV reading was recorded. Voltage reading was increasing, but was not stable. Thus small impeller was replaced and intensive mixing was provided with bigger magnetic stirrer impeller. After some time, reading was stable near 812mV with ±3mV variation. At this moment electrode was calibrated to 850mV. For air purging into water, saturated Oxygen concentration was determined using tabular data [2]. Temperature of liquid water was also recorded.

4.2.1.1. Nitrogen purging and zero calibration

Membrane was wound on cylindrical support and immersed inside the reactor. After filling reactor with distilled water, nitrogen purging started. See Fig.3 for electrode arrangement. After one hour and 15 min, transmeter reading lowered to 14mV and stable after 10 minutes. At this time, zero calibration was made. Nitrogen purging stopped and reactor inlets were toughly sealed to prevent air leaking. By starting the Peristaltic pump, liquid water saturated with oxygen passed through the membrane tube and oxygen concentration in terms of mV reading inside the bulk liquid was recorded with time.

By accepting the linear calibration curve, all mV readings can be converted into concentrations. Calibration results and mV vs. time are given in Fig.A1-1 and Fig.A1-2 respectively. Bulk oxygen concentration variation with time is given in Fig.4.

4.2.1.2. Determination of total resistance under Exp. 1TH

Membrane surface area	= 0.0671 m^2
Concentration gradient (Fig.4)	= 0.0159 (mg/l) /min
Oxygen transfer rate	= (0.0159 x 2.516)/ 0.0671 (mg/ m^2.min) = 0.5962
Total resistance (Refer to theory :Eq. 5)	= Mean conc. difference (Fig.4) / Oxygen transfer rate
	= 8.727/0.5962= 14.637 m^2.min/l = 14637.7 min/m

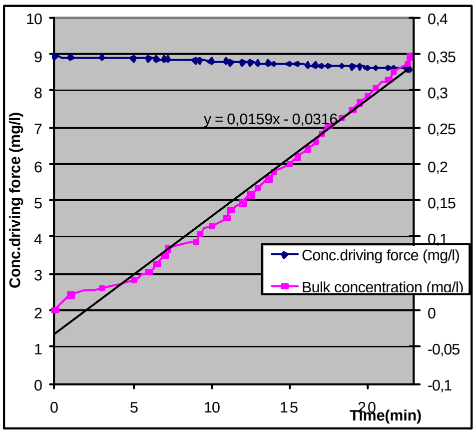


Fig.4. Concentration driving force and bulk concentration vs time under Exp. 1TH

It can be concluded from Fig.4 that the concentration driving force is uniform up to the considerable time period. Therefore oxygen can be supplied for microbial growth at a uniform rate. In order to obtain the steady state concentration difference, it would be needed to run Exp. for a long time period.

4.2.2. EXP. 2TH

Oxygen is dissolved in water by means of *pure oxygen purging.* Both oxygen dissolved water and membrane bioreactor are kept at room temperature (21°C).

While pure oxygen is being purged into water, uniform mixing was supplied with magnetic stirrer. Within short time period, transmeter showed the maximum reading (2000mV). Therefore microelectrode was calibrated for saturated oxygen in liquid water as 1975mV [Fig.A1-3 and Fig.A1-4]. Thereafter, nitrogen was purged inside bulk liquid water and after some time reading showed 7mV stable value and zero calibration was made. By transferring oxygen saturated water inside membrane, bulk oxygen concentration (mV) was recorded with time.

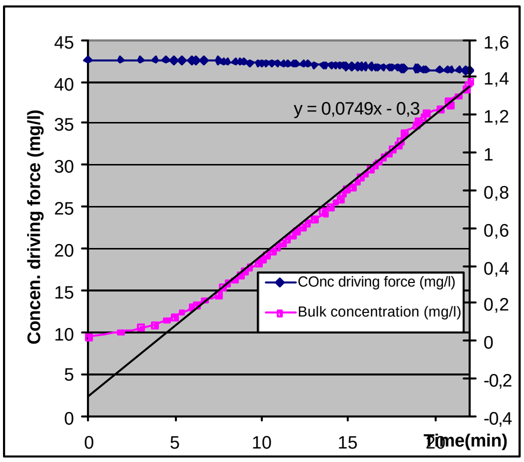


Fig.5. Concentration driving force and bulk concentration vs time under Exp. 2TH

In comparing Fig.4 and Fig.5. Under pure oxygen purging conditions, equilibrium oxygen concentration in distilled water is nearly five times higher than the air purging. Using the standard table given [2] for pure air purging at 21°C,oxygen concentration in water is 8.915 mg/l. According to the calculation based on temperature dependant Henry coefficient, saturated oxygen concentration was 42.65 mg/l which shows five times higher value confirming the experimental results.

4.2.2.2 Determination of total resistance under EXP. 2TH

Membrane surface area = $0.0671\ m^2$
Concentration gradient (Fig.5) = 0.0749 (mg/l) /min
Oxygen transfer rate = (0.0749 x 2.516)/ 0.0671 (mg/ m^2.min) = 2.80847
Total resistance (Refer to theory: Eq. 5) = Mean conc. difference (Fig.5) / Oxygen transfer rate
=41.964/ 2.80847= 14.941 m^2.min/l= 14941.93 min/m

4.2.3. Exp. 3TH

Oxygen is dissolved in water by means of *pure oxygen purging.* Both oxygen dissolved water and membrane bioreactor are kept at 55°C.

To achieve high production rate of bio gas, anaerobic processes are normally conducted at thermophilic conditions i.e. maintaining at 55°C. Therefore this Exp. was conducted to investigate effect of oxygen transfer rate at 55°C through tubular membranes. According to the calibration results, mV reading was stable at 888mV which is a lower value in comparing calibration results at room temperature. When purging nitrogen in order to make zero calibration, mV reading was stable at 17mV and then made zero calibration (Fig.A1-5&Fig.A1-6). Even though pure oxygen purged water is maintained at 55°C, cold oxygen gas caused to decrease the water temperature to 40°C. Therefore dissolved oxygen concentration was determined at 40°C.

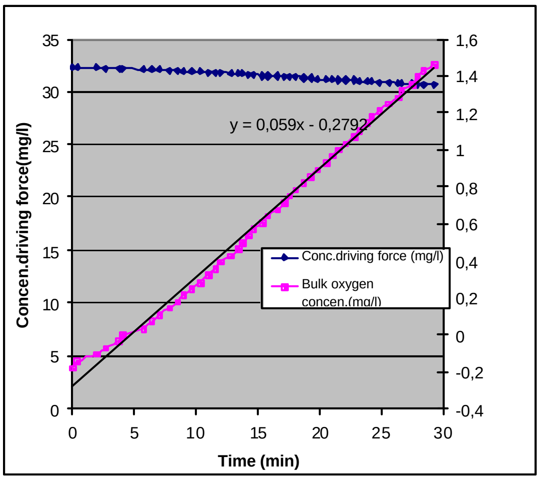


Fig.5. Bulk oxygen concentration and Concentration driving force vs time under Exp. 3TH

4.2.3.1. Determination of total resistance under EXP. 3TH

Membrane surface area = $0.0671\ m^2$
Concentration gradient (Fig.5) = 0.059 (mg/l) /min
Oxygen transfer rate = (0.059 x 2.516)/ 0.0671 (mg/ m^2.min) = 2.2122

Total resistance (Refer to theory: Eq.5) = Mean conc. difference (Fig.5) / Oxygen transfer rate
= 31.5034/ 2.2122= 14.240 m^2.min/l = 14240 min/m

Both Exp. 2TH and 3TH shows no significant variation of total resistance. Solubility of oxygen in water decreases with increase in temperature. Therefore lower flux in 3TH is due to the decrease in concentration driving force caused by low solubility of oxygen at elevated temperatures.

4.2.4.1. Exp. 4TH

Oxygen is dissolved in water by means of *<u>pure oxygen purging.</u>* Oxygen dissolved water is kept at 21°C while membrane bioreactor being at 55°C.

When purging pure oxygen at room temperature, mV reading was stable around 1288 mV and calibrated as 1300mV. (Fig.A1-7 and Fig.A1-8)

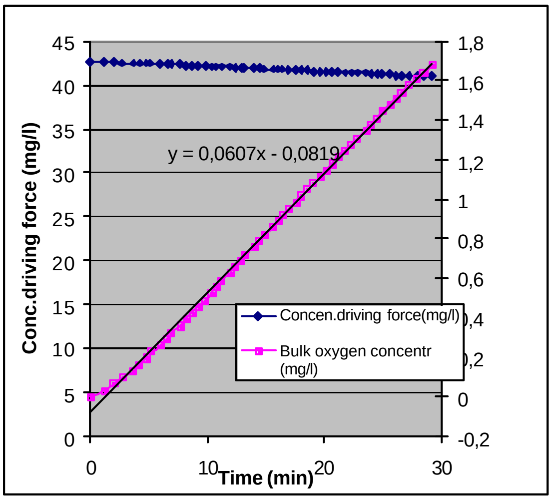


Fig.6. Bulk oxygen concentration and concentration driving forces vs time under Exp. 4TH

4.2.4.1 Determination of total resistance under EXP. 4TH

Membrane surface area	= 0.0671 m^2
Concentration gradient (Fig.6)	= 0.0607 (mg/l) /min
Oxygen transfer rate	= (0.0607 x 2.516)/ 0.0671 (mg/ m^2.min) = 2.276
Total resistance (Refer to theory :Eq.5)	= Mean conc. Difference (Fig.6) / Oxygen transfer rate = 41.8136/ 2.276= 18.371m2.min/l = 18371 min/m

It gives a convincing conclusion, in comparing the resistances obtain under Exp. 2 and Exp.4. In this situation, supply conditions of pure oxygen into water are identical, but membranes are held at different temperatures. There are no significant change of permeabilities and selectivities of O_2 and N_2 in standard PDMS membranes within temperature range at which these Experiments are conducted [8]. In Exp. 4^{TH}, increase of dissolved O_2 concentration in bulk water is lower than that of 2TH. Due to large driving force, it is expected to have high flux in 4^{TH}, but lower flux in Exp. May be due to high boundary layer resistance in bulk water side of tubular membrane.

4.2.5. Exp. 5TH

Oxygen is dissolved in water by means of *<u>pure air purging</u>*. Oxygen dissolved water is kept at 19°C while membrane bioreactor being kept at 55°C.

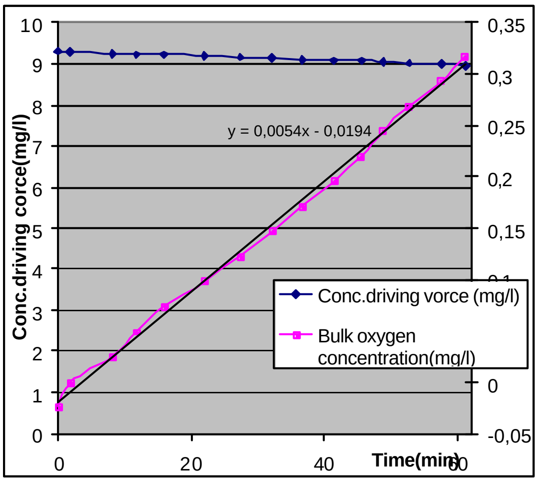


Fig.7. Bulk oxygen concentration and concentration driving forces vs time under Exp. 5TH

4.2.5.1. Determination of total resistance under EXP. 5TH

Membrane surface area	= 0.0671 m^2
Concentration gradient (Fig.7**)**	= 0.0054 (mg/l) /min
Oxygen transfer rate	= (0.0054 x 2.515)/ 0.0671(mg/ m^2.min) = 0.202399
Total resistance (Refer to theory: Eq.5)	= Mean conc. difference (Fig.7) / Oxygen transfer rate
	= 9.1296/ 0.202399= 45,106m^2.min/l = 45106 min/m

Solubility and diffusivity of oxygen and nitrogen gases show no remarkable increase with temperature in PDMS. Also there is no coupling effect of two gases inside the membrane. Bulk water is saturated with nitrogen and inner surface of membrane is covered with more nitrogen molecules because of air purging. This causes low solubility of oxygen leading to low oxygen transfer rate. Large total flow resistance is due to the lower oxygen transfer rate due to above phenomena.

5. Experiments using thin tubular membrane

5.1. Definitions of Experiments

In addition to the five similar Experiments which were conducted with thick membrane, additional two Experiments are defined for thin membrane. In order to investigate the repeatability of experiments, Exp. 1TN and Exp. 2TN are repeated. Table 2 gives the details under thin membrane experiments.

Table2. Definitions of experiments under thin membrane.

	Thin membrane		
Experiment	Temperature (°C)		
	Membrane bioreactor	Oxygen dissolved water	Oxygen supply method
Exp. 1TN	20	20	Air purging
Exp. 2TN	20	20	Oxygen purging
Exp. 3TN	55	40	Oxygen purging
Exp. 4TN	55	21	Oxygen purging
Exp. 5TN	55	19	Air purging

Exp. 6TN	20	40	Oxygen purging
Exp. 7TN	22.5	**Air at 22.5 is passed through membrane**	
Repeated Experiments			
Exp. 1RTN	18	18	Air purging
Exp. 2RTN	18	18	Oxygen purging

5.2. Results and discussion under different experiments

It was necessary to see the behaviour of the mV reading against oxygen concentration. Therefore by purging pure oxygen and air separately, stable readings were recorded and these are shown together with corresponding calibrated results in Fig.A2-1. It can be seen that nearly linear behaviour of these parameters.

5.2.1. Exp. 1TN

Oxygen is dissolved in water by means of <u>air purging.</u> Both water and membrane bioreactor are kept at room temperature (20°C).

Electrode calibration results are given in Fig.A2-2 and Fig.A2-3.

5.2.1.1. Determination of total resistance under EXP. 1TN for thin membrane

Length of thin membrane used	= 2.75m
External diameter of tubular membrane	= 3mm = 0.003m
Volume of water in the reactor	= 1.57 l
Membrane surface area	= 0.02592 m^2
Concentration gradient (Fig.8)	= 0.0149 (mg/l) /min
Oxygen transfer rate	= (1.57 x0.0149)/0.02592 (mg/ m^2.min) = 0.90250
Total resistance (Refer to theory: Eq.5)	= Mean conc. difference (Fig.8) / Oxygen transfer rate = 8.9408/ 0.90250= 9.90670m2.min/l = 9906.70 min/m

As expected results show the lower membrane resistance than thick membrane used in the earlier experiments.

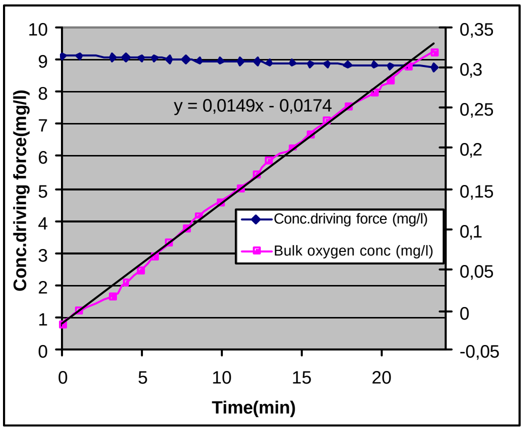


Fig.8. Bulk oxygen concentration and concentration driving forces vs time under Exp. 1TN

5.2.2. Exp. 2TN

Oxygen is dissolved in water by means of <u>pure oxygen purging.</u> Both water and membrane bioreactor are kept at room temperature (20°C):
Electrode calibration results and mV vs Time results are given in Fig.A2-4 & Fig.A2-5. respectively

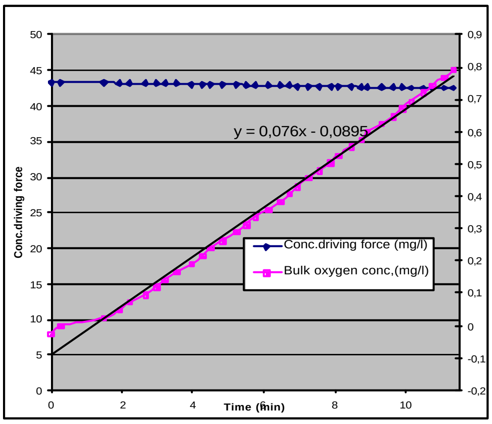


Fig.9. Bulk oxygen concentration and concentration driving forces vs time under Exp. 2TN

5.2.2.1. Determination of total resistance under EXP. 2TN for thin membrane

Length of thin membrane used = 2.75m
External diameter of tubular membrane = 3mm = 0.003m
Volume of water in the reactor = 1.57 l
Membrane surface area = 0.02592 m^2
Concentration gradient (Fig.9) = 0.076 (mg/l) /min
Oxygen transfer rate = (1.57 x0.076)/0.02592 (mg/ m^2.min) = 4.603395
Total resistance (Refer to theory: Eq.5) = Mean conc. difference (Fig.9) / Oxygen transfer rate
= 42.876/ 4.603395= 9.3139 m^2.min/l= 9313.9 min/m

As evidenced by thick membrane Exp. 1TH &2TH, thin membrane Exp. 1TN& 2TN show the five times increase of oxygen flux.

5.2.3. Exp. 3TN

Oxygen is dissolved in water by means of <u>pure oxygen purging.</u> Both water and membrane bioreactor are kept at 55°C
Electrode calibration results and mV vs Time results are given in Fig: A2-6 & Fig.A2-7 respectively.

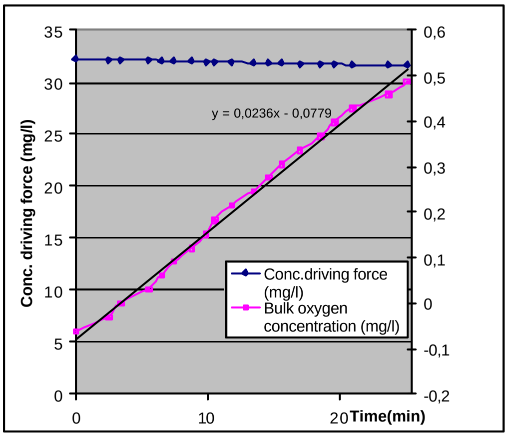


Fig.10. Bulk oxygen concentration and concentration driving forces vs time under Exp. 3TN

5.2.3.1. Determination of total resistance under EXP. 3TN for thin membrane

Length of thin membrane used = 2.75m
External diameter of tubular membrane = 3mm = 0.003m
Volume of water in the reactor = 1.57 l
Membrane surface area = 0.02592 m^2
Concentration gradient (Fig.10) = 0.0236 (mg/l) /min
Oxygen transfer rate = (1.57 x0.0236)/0.02592 (mg/ m^2.min) = 1,4295
Total resistance (Refer to theory: Eq.5) = Mean.conc. Difference (Fig.10) / Oxygen transfer rate = 31.9318/1.4295 = 22.337 m^2.min/l
= 22337 min/m

In comparing the flux and resistance of Exp. 2TH & 3TH, flux reduction(21%) was due to the low driving force, By contrast, under similar conditions, flux reduction (68%) in Exp. 2TN & 3TN was due to the increase of reactor boundary layer resistance leading to the increase in total flow resistance.

5.2.4. Exp. 4TN.

Oxygen is dissolved in water by means of pure oxygen purging. Oxygen dissolved water is kept at 21°C while membrane bioreactor being kept at 55°C.

Electrode calibration results and mV vs Time results are given in Fig:A2-8 & Fig.A2.9 respectively

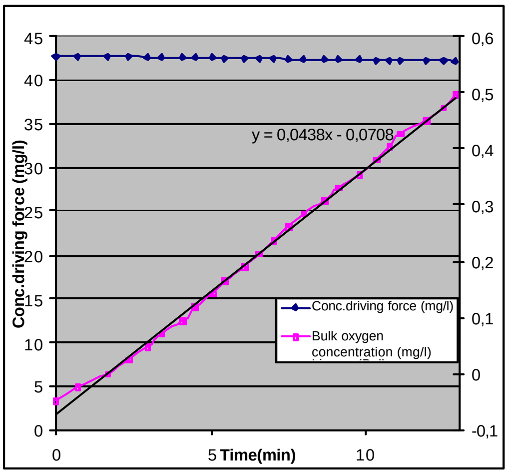


Fig.11. Bulk oxygen concentration and concentration driving forces vs time under Exp. 4TN

5.2.4.1. Determination of total resistance under EXP. 4TN for thin membrane

Length of thin membrane used = 2.75m
External diameter of tubular membrane = 3mm = 0.003m
Volume of water in the reactor = 1.44 l (This volume is little lower than the water volume(1.57) used in Exp.1 and Exp.2 because of leaving reactor content open inside autoclave about one and half days)
Membrane surface area = 0.02592 m^2
Concentration gradient (Fig.11) = 0.0438 (mg/l) /min
Oxygen transfer rate = (1.44 x0.0438)/0.02592 (mg/ m^2.min) = 2.4333
Total resistance (Refer to theory: Esq. 5) = Mean conc. difference (Fig.11) / Oxygen transfer rate = 42.436/ 2.4333= 17.4396 m^2.min/l = 17439.6 min/m

Based on the similar argument made for results in Exp. 2TH & 4TH, increase of total resistance in Exp. 4TN is due to the boundary layer resistance in side the membrane bioreactor.

5.2.5. Exp. 5TN

Oxygen is dissolved in water by means of <u>air purging:</u> Oxygen dissolved water is kept at 19°C while membrane bioreactor being kept at 55°C:

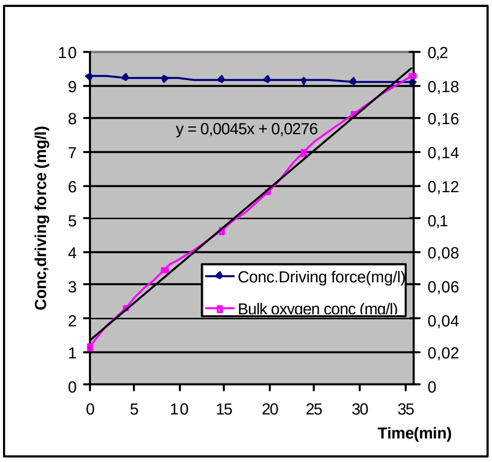


Fig.12. Bulk oxygen concentration and concentration driving forces vs time under Exp. 5TN

Electrode calibration results and mV vs Time results are given in Fig:A2-10 & Fig.A2-11, respectively

5.2.5.1. Determination of total resistance under EXP. 5TN for thin membrane

Length of thin membrane used	= 2.75m
External diameter of tubular membrane	= 3mm = 0.003m
Volume of water in the reactor	= 1.720 l
Membrane surface area	= 0.02592 m^2
Concentration gradient (Fig.12)	= 0.0045 (mg/l) /min
Oxygen transfer rate	= (1.7201 x0.0045)/0.02592 (mg/ m^2.min)
	= 0.2986(mg/ m^2.min)
Total resistance (Refer to theory: Eq.5)	= Mean conc. difference (Fig.12) / Oxygen transfer rate
=	9.1716/ 0.2986= 30.715m^2.min/l= 30715 min/m

5.2.6. Exp. 6TN.

Oxygen is dissolved in water which is at 55°C by means of pure <u>oxygen purging.</u> Membrane bioreactor is kept at 20°C

Electrode calibration results and mV vs Time results are given in Fig:A2-12.& Fig.A2-13. respectively

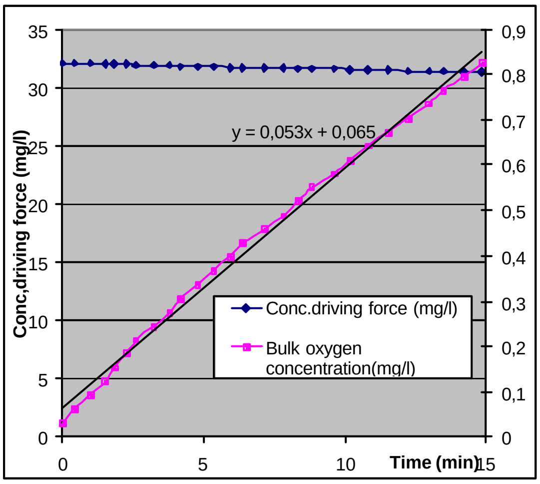


Fig.13. Bulk oxygen concentration and concentration driving forces vs time under Exp. 6TN

5.2.6.1. Determination of total resistance under EXP. 6TN for thin membrane

Length of thin membrane used	= 2.75m
External diameter of tubular membrane	= 3mm = 0.003m
Volume of water in the reactor	= 1.795
Membrane surface area	= 0.02592 m^2
Concentration gradient (Fig.13)	= 0.053 (mg/l) /min
Oxygen transfer rate	= (1.795 x0.053)/0.02592 (mg/ m^2.min)
	= 3,6703(mg/ m^2.min)
Total resistance (Refer to theory: Eq.5)	= Mean conc. difference (Fig.13) / Oxygen transfer rate
	= 31,7176/ 3,6703= 8,641m^2.min/l
	= 8641 min/m

5.2.7. Exp. 7TN

Membrane bioreactor is at room temperature (22.5°C) and ONLY AIR at room temperature is passed through the membrane.
Electrode calibration results and mV vs Time results are given in Fig:A2-14 & Fig.A2-15 respectively

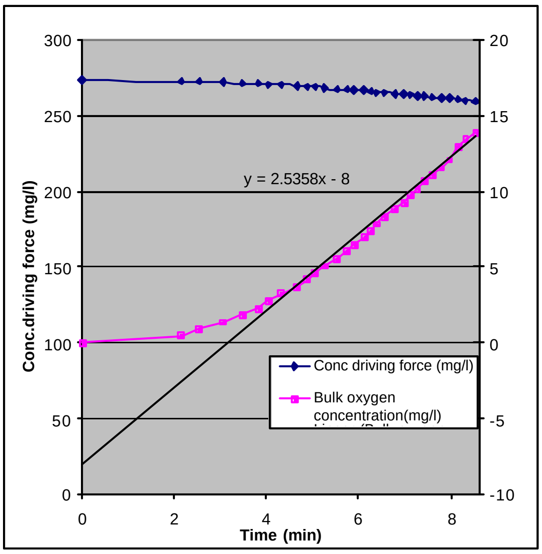


Fig.14. Bulk oxygen concentration and concentration driving forces vs time under Exp. 7TN

5.2.7.1. Determination of total resistance under EXP. 7TN for thin membrane

Length of thin membrane used	= 2.75m
External diameter of tubular membrane	= 3mm = 0.003m
Volume of water in the reactor	= 1.57 l
Membrane surface area	= 0.02592 m^2
Concentration gradient (Fig.14)	= 2.5358 (mg/l) /min
Oxygen transfer rate	= (1.795 x2.5358)/0.02592 (mg/ m^2.min)
	= 175.60(mg/ m^2.min)
Total resistance (Refer to theory: Eq.5)	= Mean conc. difference (Fig.14) / Oxygen transfer rate
	= 266.73/ 175.60 = 1,518m^2.min/l
	= 1518 min/m

Supply of air without dissolving in water eliminates the inside boundary layer of tubular membrane and also improve the solubility due to the absence of liquid water. Therefore large flux is due to the lower total resistance.

6. Repetition of thin membrane experiments under Exp. 1TN and Exp.2TN

Objective of this Exp. is to investigate the ability of reproducing the results obtained under Exp. 1TN and Exp. 2TN for thin membranes. Therefore experiments were conducted using both air and oxygen purging at room temperature. Linear variation of electrode calibration results can be noticed in Fig.A3-1.

6.1. Exp. 1RTN

Oxygen is dissolved in water by means of air purging. Both oxygen dissolved water and membrane bioreactor are kept at room temperature (18°C).

It should be noted that experiments were conducted under the identical conditions used in Exp. 1TN and Exp. 2TN except the room temperature which slightly varies under atmosphere conditions. Due to this reason, Exp. 1TN was conducted at 18°C instead of 20°C.Electrode calibration results and mV vs Time results are given in Fig.A3-2 & Fig.A3-3 respectively.

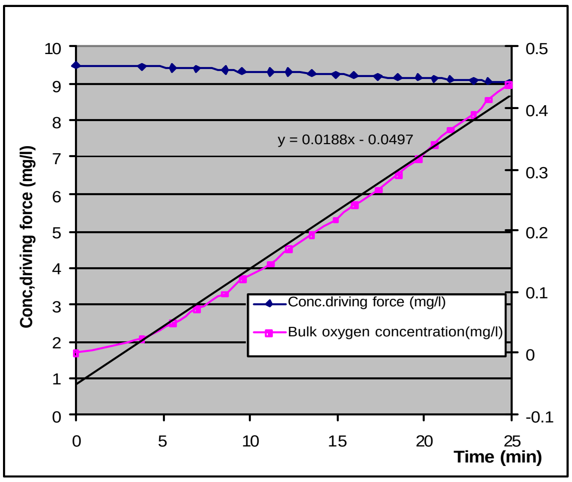


Fig.15. Bulk oxygen concentration and concentration driving forces vs time under Exp. 1RTN

6.1.1. Determination of total resistance under EXP. 1RTN for thin membrane

Length of thin membrane used	= 2.75m
External diameter of tubular membrane	= 3mm = 0.003m
Volume of water in the reactor	= 1.57 l
Membrane surface area	= 0.02592 m^2
Concentration gradient (Fig.15)	= 0.0188 (mg/l) /min
Oxygen transfer rate	= (1.57 x0.0188)/0.02592 (mg/ m^2.min)
	= 1.1387(mg/ m^2.min)
Total resistance (Refer to theory: Eq.5)	= Mean conc. difference (Fig.15) / Oxygen transfer rate
	= 9.2483/ 1.1387= 8.1218m^2.min/l = = 8121.8 min/m

6.2. Exp. 2RTN

Oxygen is dissolved in water by means of <u>pure oxygen purging.</u> Both oxygen dissolved water and membrane are kept at room temperature (18°C)

Electrode calibration results and mV vs Time results are given in Fig.A3-4 and Fig.A3-5 respectively

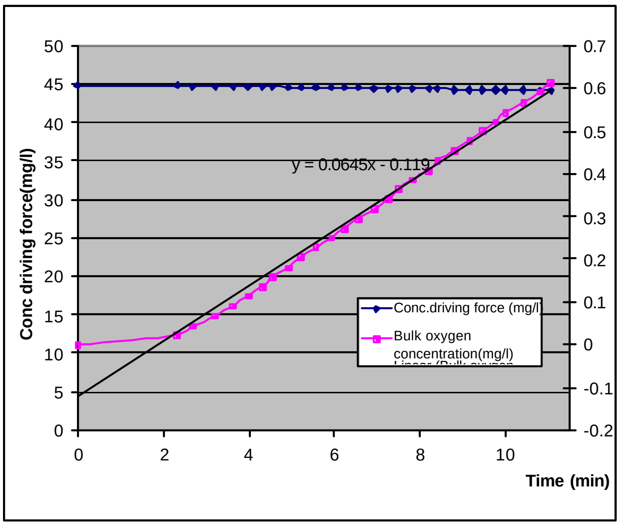


Fig.16. Bulk oxygen concentration and concentration driving forces vs time under Exp. 1RTN

6.2.1. Determination of total resistance under EXP. 2RTN for thin membrane

Length of thin membrane used	= 2.75m
External diameter of tubular membrane	= 3mm = 0.003m
Volume of water in the reactor	= 1.57 l
Membrane surface area	= 0.02592 m^2
Concentration gradient (Fig.16)	= 0.0645 (mg/l) /min
Oxygen transfer rate	= (1.57 x0.0645)/0.02592 (mg/ m^2.min)
	= 3.9068 (mg/m2,min)
Total resistance (Refer to theory: Eq.5)	= Mean conc. difference (Fig.16) / Oxygen transfer rate
	= 44.43/3.9068 = 11.372m^2.min/l = 11372 min/m

7. Errors and remedial actions to improve experimental results

In removing all dissolved oxygen by purging nitrogen into reactor vessel there is a possibility of leaking air into the reactor head space leading some inaccuracies in zero calibration. Also when purging pure oxygen into the open beaker, it should be thoroughly covered to prevent mixing with air in order to maintain pure oxygen partial pressure 1 atm above liquid surface. Otherwise this will lead to the inaccurate calculation of dissolved equilibrium concentration in water. Variation of room temperature during the experiments caused some errors in estimating dissolved oxygen concentration. Microelectrode used in these experiments is very vulnerable to external environmental conditions. Following the completion of experiments with thick membrane, electrode was left in water about four days before starting the next set of readings. When using this electrode, too low values of mV reading under pure oxygen purging conditions and even under air purging conditions were found. It was noticed that no filling solution inside electrode chamber. This may be due to immersed in water for long time and diffusion of solution through thin membrane covered. Filling with new solution and replaced with new membrane could recover original performance. Under pure oxygen purging conditions, sometimes, electrode reading achieved maximum transmeter reading (2000mV) within short time. It would be better to use pH meter with wide maximum mV range.

8. Summary of the results.

Results obtained under both thick and thin membranes are summarized in Table 4.

Table 4. Summary of results

Thick membrane					
Experiment	Temperature (°C)				
	Membrane bioreactor	**Oxygen dissolved water**	**Oxygen Supply method**	**Oxygen transfer Rate (mg/m^2.min)**	**Total resistance (min/m**
Exp. 1TH	21	21	Air purging	0.5962	14637
Exp. 2TH	21	21	Oxygen purging	2.808	14941
Exp. 3TH	55	40	Oxygen purging	2.212	14240
Exp. 4TH	55	21	Oxygen purging	2.276	18371
Exp. 5TH	55	19	Air purging	0.20239	45106
Thin membrane					
Experiment	Temperature (°C)				
	Membrane bioreactor	**Oxygen dissolved water**	**Oxygen Supply method**	**Oxygen transfer Rate (mg/m^2.min)**	**Total resistance (min/m**
Exp. 1TN	20	20	Air purging	0.90250	9906
Exp. 2TN	20	20	Oxygen purging	4.6033	9313
Exp. 3TN	55	40	Oxygen purging	1,4295	22337
Exp. 4TN	55	21	Oxygen purging	2.4333	17439
Exp. 5TN	55	19	Air purging	0,2986	30715
Exp. 6TN	20	40	Oxygen purging	3,6703	8641

Exp. 7TN	22.5	22.5	ONLY Air supplied	175.60	1518
Repeated experiments for thin membrane					
Exp. 1RTN	18	18	Air purging	1.1387	8121
Exp. 2RTN	18	18	Oxygen purging	3.9068	11372

9. Variation of oxygen flux with total resistance in thick and thin tubular membranes

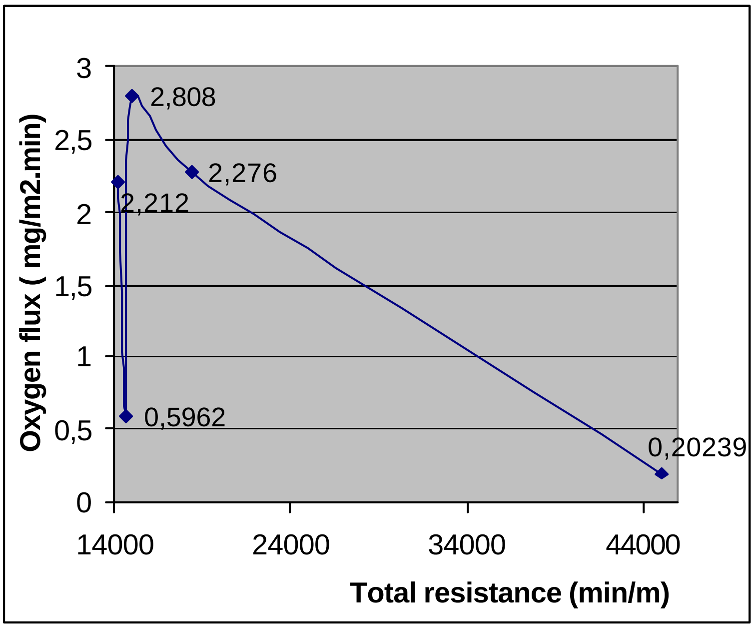


Fig.17. Oxygen flux vs total resistance for thick tubular membrane

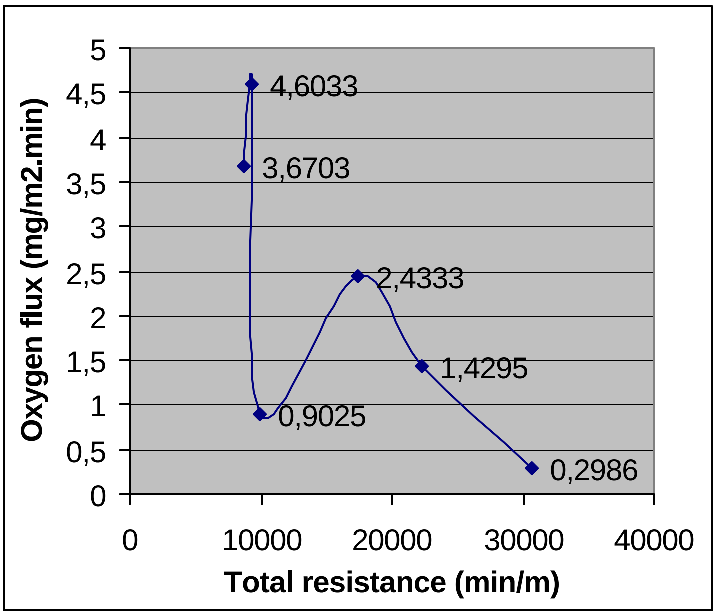


Fig.18. Oxygen flux vs total resistance for thin tubular membrane

10. Conclusions

At room temperature, both thin and thick membranes produced the lowest oxygen transfer rates when air saturated water was supplied inside the membranes. Highest oxygen transfer rate and the lowest total transport resistance were reported when pure air was supplied inside membranes. When water saturated with pure oxygen is pumped inside thick and thin membranes at room temperature, the next highest oxygen transfer rates across membranes were reported (Fig.17 & Fig.18). When the reactor was held at 55^0C both membranes showed a reduction of oxygen transfer rate compared to the room temperature experiments. If the oxygen demand (mg/d) of the biological medium is known, one can select the appropriate experimental strategy and estimate the required membrane length using the experimental results. Mixing method in terms of impeller type and rpm has significant impact to the transport resistance and flux. When investigating the repeatability of the experiments with thin membrane under Exp. 1TN & 2TN, consistent results were found. Exp. 1RTN could produce the oxygen transfer rates within 26% error and Exp. 2RTN within 15% error. Supply of only pure air(not dissolved in water) through thin membranes shows the lowest total resistance and the highest flux. This strategy is normally not recommended for microaerobic oxygen supply situations.

11. References

1. G. Tchobanoglous, F.L. Burton, H.D. Stensel, Waste water engineering: Treatment and Reuse , 4th Edition, Metcalf & Eddy Inc, McGraw-Hill, 2003.

2. A.D. Eaton, L.S. Clesceri, A.E. Greenberg, Standard methods for the examination of water and waste water, 19th Edition, American Public Health Association, 1995.

3. M. Mulder, Basic principles of membrane technology**,** **2**nd Edition, Kluwer Academic Publishers, 1996.

4. P. Pandey, R.S. Chauhan, Membranes for gas separation, Prog. Polym. Sci. 26(2001) 853 - 893.

5. M.W. Reij, J.T.F. Keurentjes, S. Hartmans, Membrane bioreactors for waste gas treatment (Mini review), Journal of Biotechnology 59 (1998) 155 – 167.

6. R. Rautenbach, R.Albrecht, Membrane Processes, Chichester: Wiley, 1989.

7. T. Stephenson, S. judd, B. Jefferson, K. Brindle, Membrane bioreactors for wastewater treatment**,** IWA publishing, 2000.

8. M.-B. Hägg, Membrane purification of Cl_2 gas - I. Permeabilities as a function of temperature for Cl2,O2,N2,H2 in two types of PDMS membranes, J.Membr. Sci. 170(2000) 173-190.

12. Appendix A

12.1. Appendix A1: Electrode calibration results for thick membrane

12.1.1. Exp. 1TH

Oxygen is dissolved in water by means of air purging and both water and membrane are kept at room temperature (21°C)

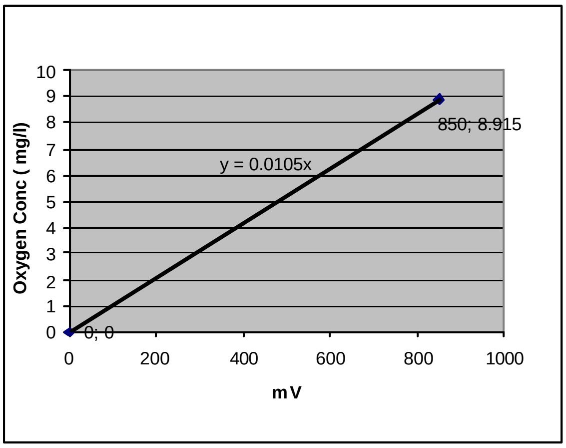


Fig.A1-1. Electrode calibration results for Exp. 1TH

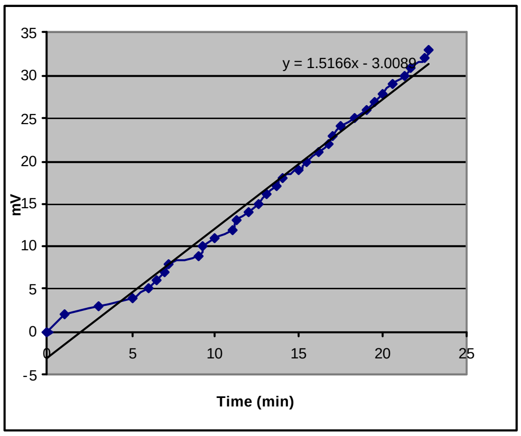


Fig.A1-2. mV vs Time (min) for Exp. 1TH

12.1.2. Exp. 2TH

Oxygen is dissolved in water by means of *<u>pure oxygen purging.</u>* Both oxygen dissolved water and membrane bioreactor are kept at room temperature (21°C):

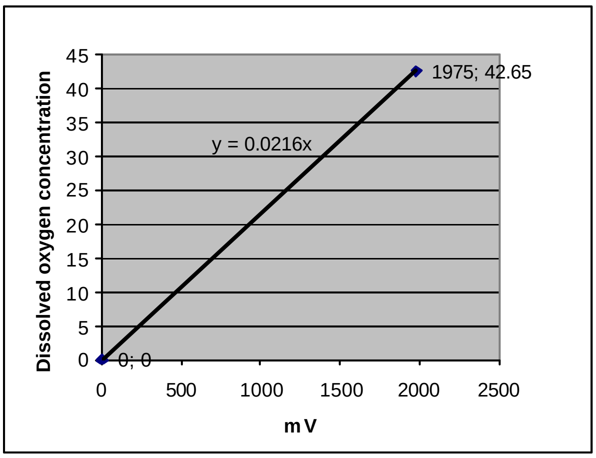


Fig.A1-3. Electrode calibration results for Exp. 2TH

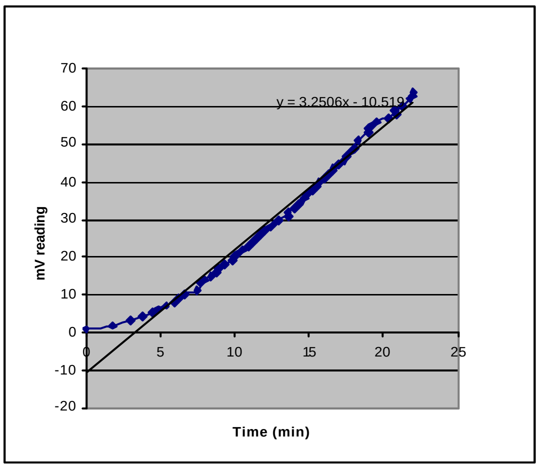
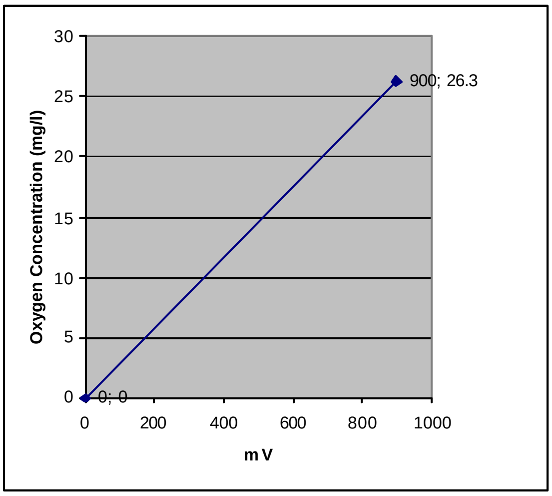


Fig.A1-4. mV vs Time (min) for Exp. 2TH

12.1.3. Exp. 3TH

Oxygen is dissolved in water by means of *pure oxygen purging.* Both oxygen dissolved water and membrane bioreactor are kept at 55°C:



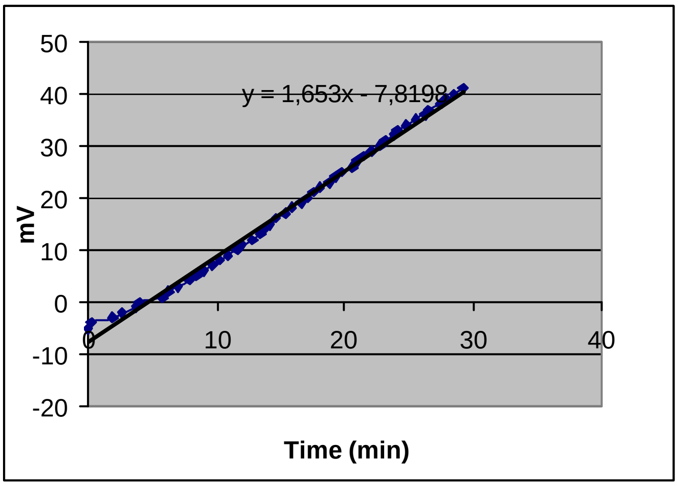
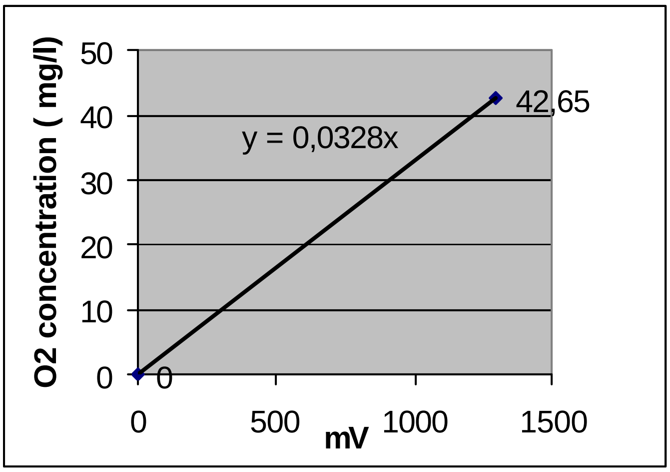


Fig.A1-5. Electrode calibration results for Exp. 3TH

Fig.A1-6. mV vs Time (min) for Exp. 3TH

1.1.4. Exp. 4TH

Oxygen is dissolved in water by means of *pure oxygen purging.* Oxygen dissolved water is kept at 21°C while membrane bioreactor being at 55°C.



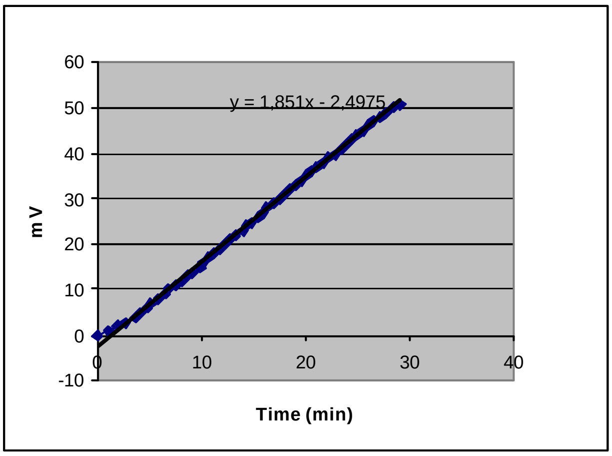
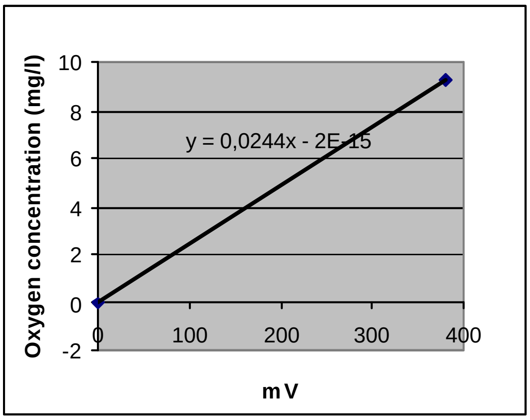


Fig.A1-7. Electrode calibration results for Exp. 4^{TH}

Fig.A1-8. mV vs Time (min) for Exp. 4^{TH}

1.2.1.5. Exp. 5TH

Oxygen is dissolved in water by means of *pure air purging*. Oxygen dissolved water is kept at 19°C while membrane bioreactor being kept at 55°C:



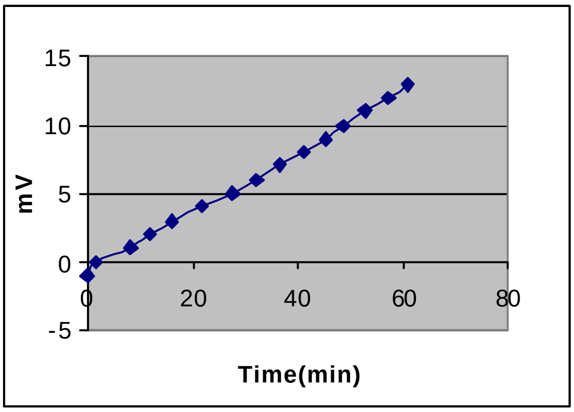


Fig.A1-9. Electrode calibration results for Exp. 5TH

Fig.A1-10. mV vs Time (min) for Exp. 5TH

12.2. Appendix A2: Electrode calibration results for thin membrane

12.2.1. Exp. 1TN

Oxygen is dissolved in water by means of air purging. Both water and membrane bioreactor are kept at room temperature (20°C)

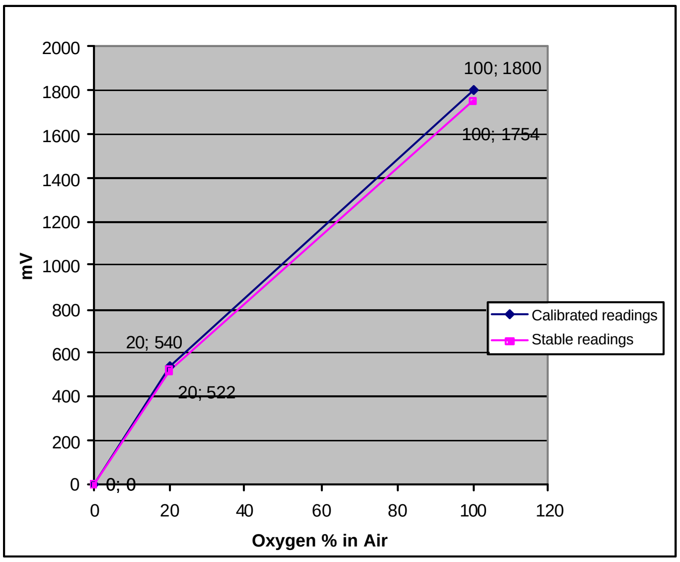


Fig.A2-1. Calibrated and stable mV reading vs oxygen percentage of air for thin membrane Experiments at room temperature

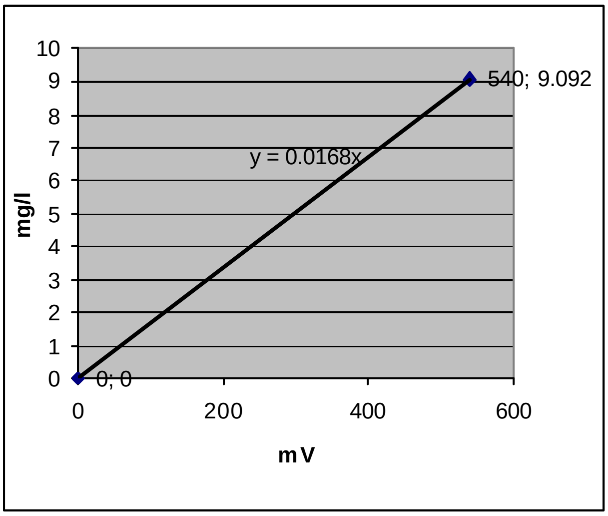


Fig.A2-2. Electrode calibration results for Exp. 1TN

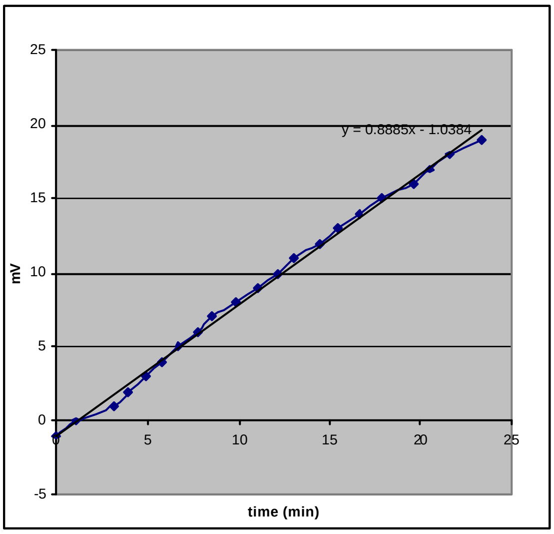


Fig.A2-3. mV vs Time (min) for Exp. 1TN

12.2.2. Exp. 2TN

Oxygen is dissolved in water by means of pure oxygen purging. Both water and membrane bioreactor are kept at room temperature (20°C)

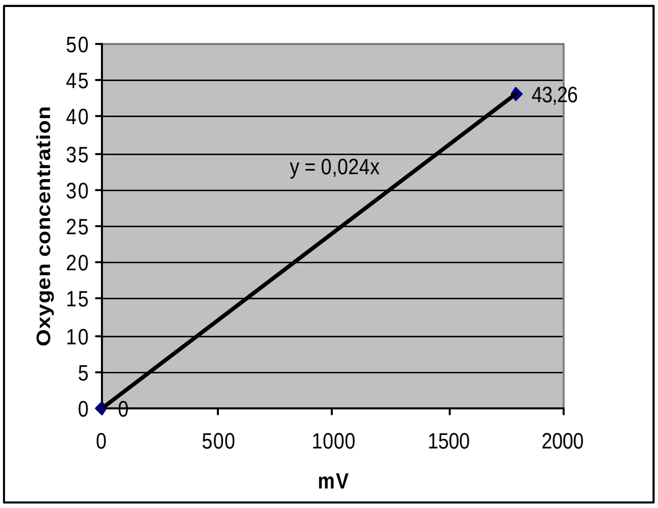


Fig.A2-4. Electrode calibration results for Exp. 2TN

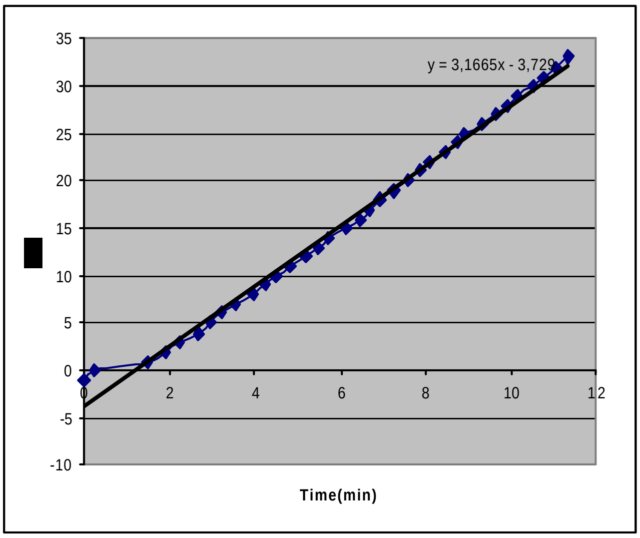
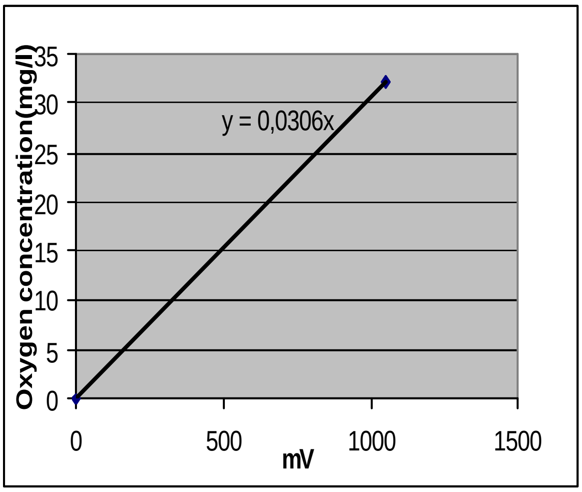


Fig.A2-5. mV vs Time (min) for Exp. 2TN

1.2.3. Exp. 3TN

Oxygen is dissolved in water by means of <u>pure oxygen purging.</u> Both water and membrane bioreactor are kept at 55°C



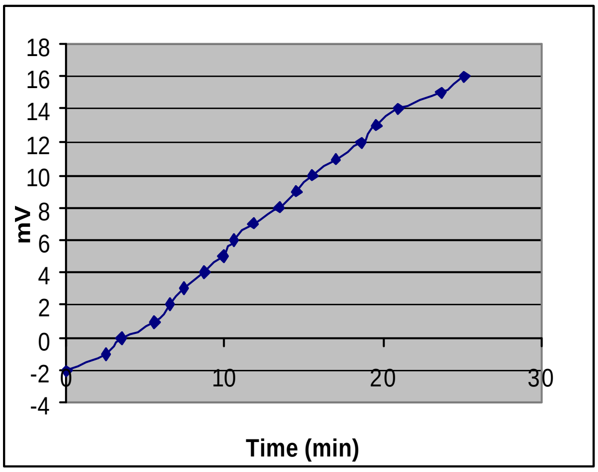
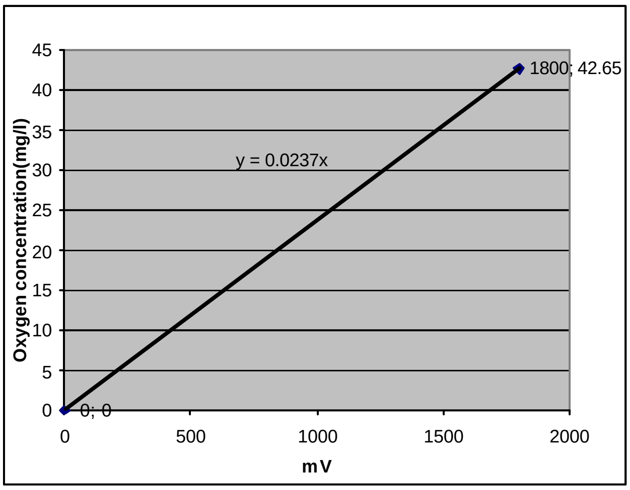


Fig.A2-7. mV vs Time (min) for Exp. 3TN

Fig.A2-6. Electrode calibration results for Exp. 3TN

1.2.2.4. Exp. 4TN

Oxygen is dissolved in water by means of <u>pure oxygen purging.</u> Oxygen dissolved water is kept at 21°C while membrane bioreactor being kept at 55°C



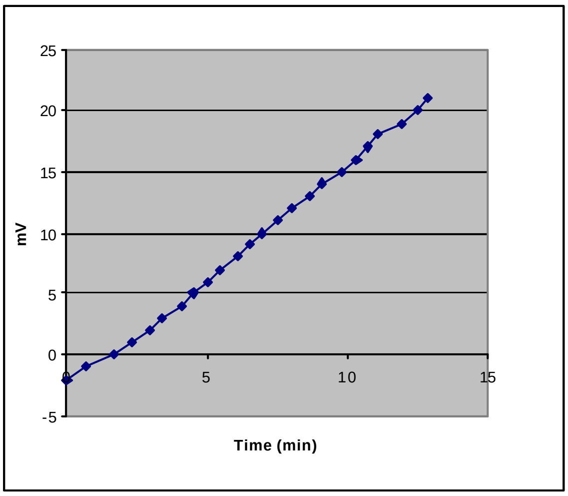


Fig.A2-8. Electrode calibration results for Exp. 4TN

Fig.A2-9. mV vs Time (min) for Exp. 4TN

12.2.5. Exp. 5TN

Oxygen is dissolved in water by means of <u>air purging:</u> Oxygen dissolved water is kept at 19°C while membrane bioreactor being kept at 55°C

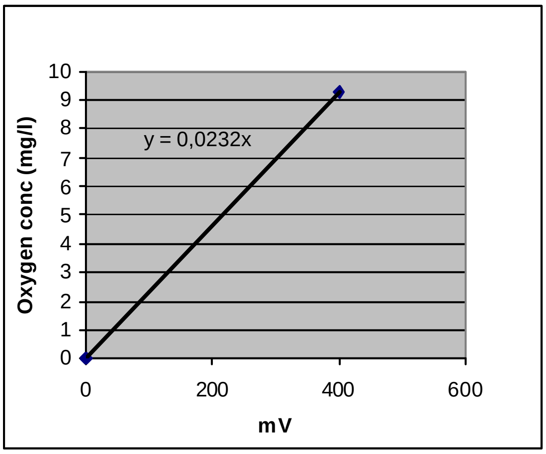


Fig.A2-10. Electrode calibration results for Exp. 5TN

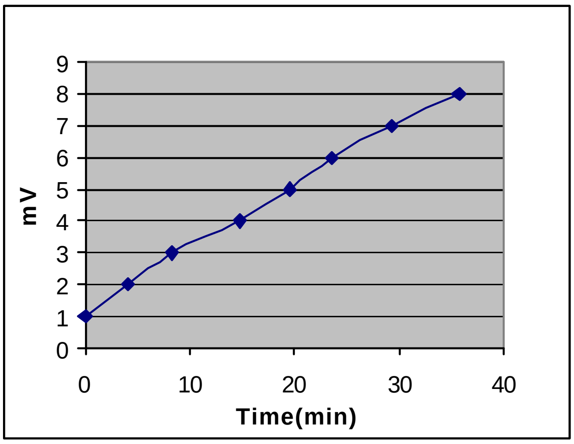


Fig.A2-11. mV vs Time for Exp. 5TN

12.2.6. Exp. 6TN

Oxygen is dissolved in water which is at 55°C by means of pure <u>oxygen purging.</u> Membrane bioreactor is kept at 20°C

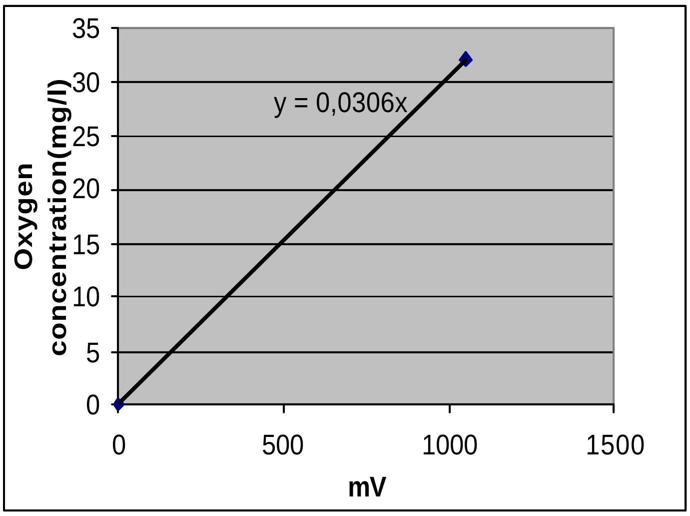


Fig.A2-12. Electrode calibration results for Exp. 6TN

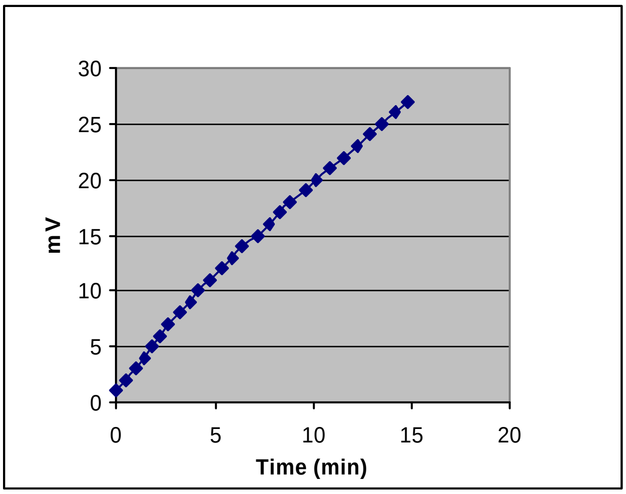


Fig.A2-13. mV vs Time (min) for Exp. 6TN

12.2.7. Exp. 7TN

Membrane immersed reactor is at room temperature(22.5°C) and ONLY AIR at room temperature is passed through the membrane.

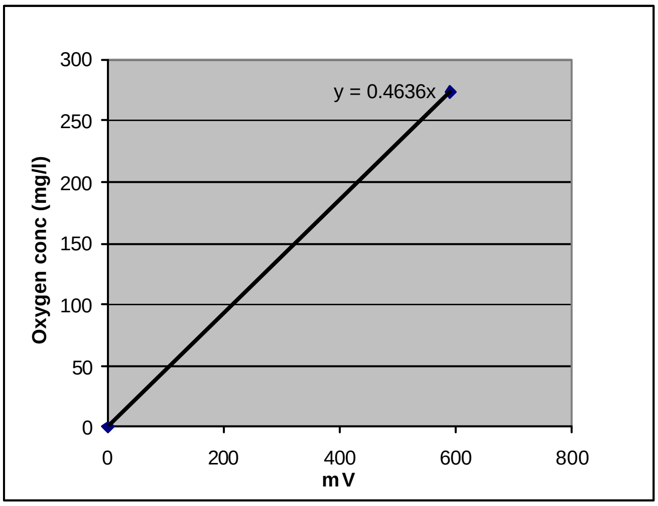


Fig.A2-14. Electrode calibration results for Exp. 7TN

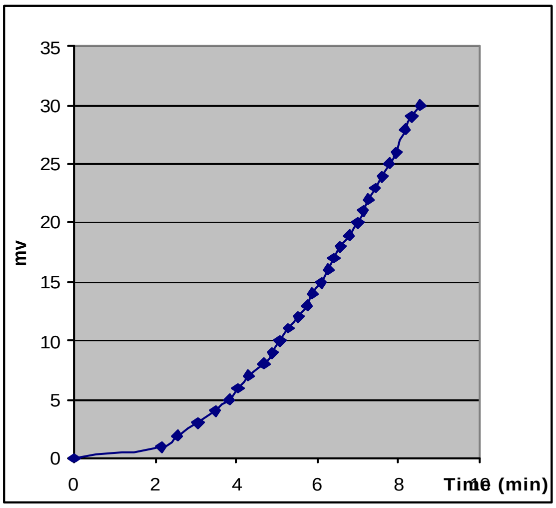


Fig.A2-15. mV vs Time (min) for Exp. 7TN

12.3. Appendix A3: Electrode calibration results for repeated experiments using thin membrane

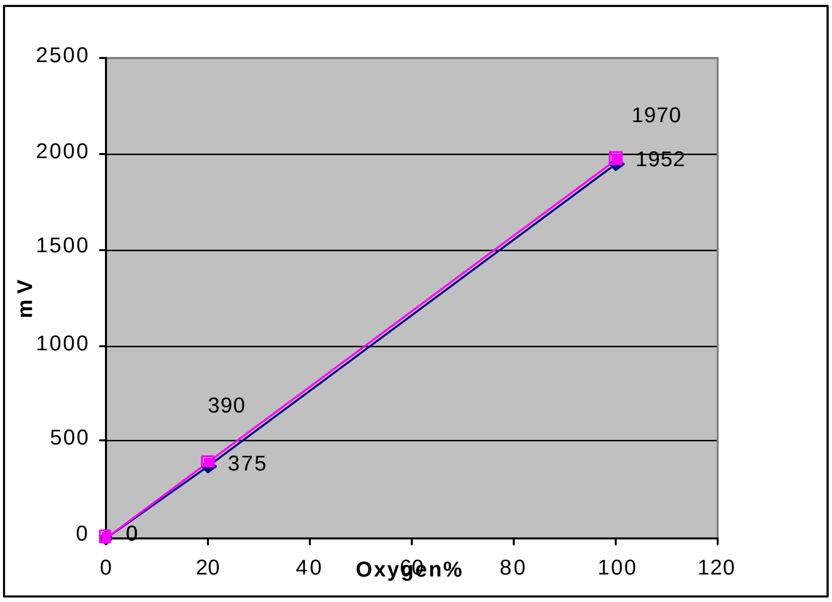
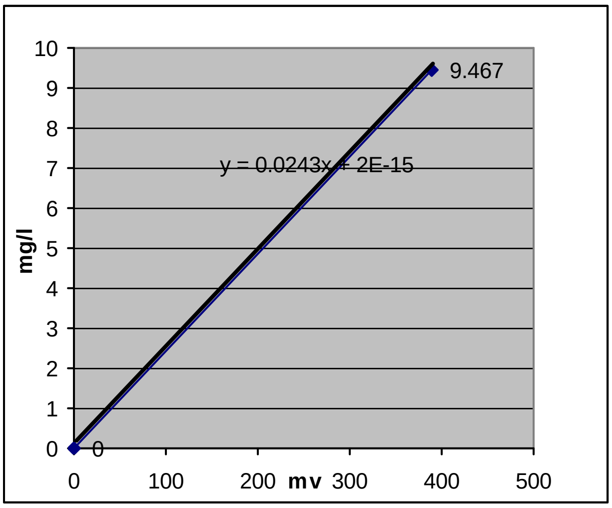


Fig. A3-1. Calibrated and stable mV reading vs oxygen percentage of air for thin membrane repeat Experiments at room temperature

12.3.1. Exp. 1RTN

Oxygen is dissolved in water by means of air purging and both oxygen dissolved water and membrane bioreactor are kept at room temperature (18^0C)



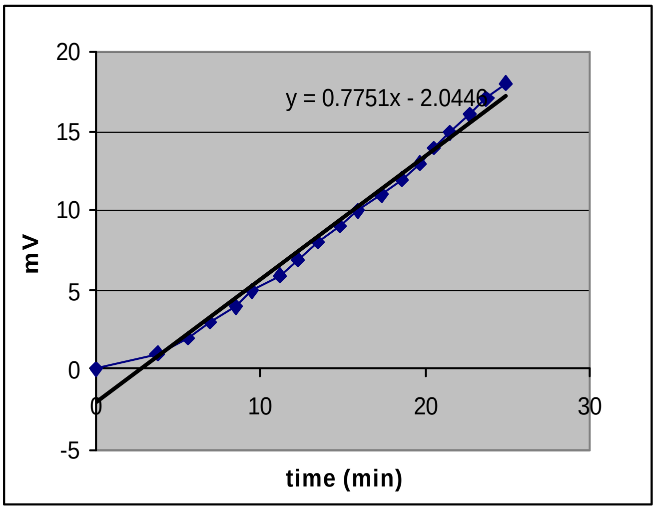
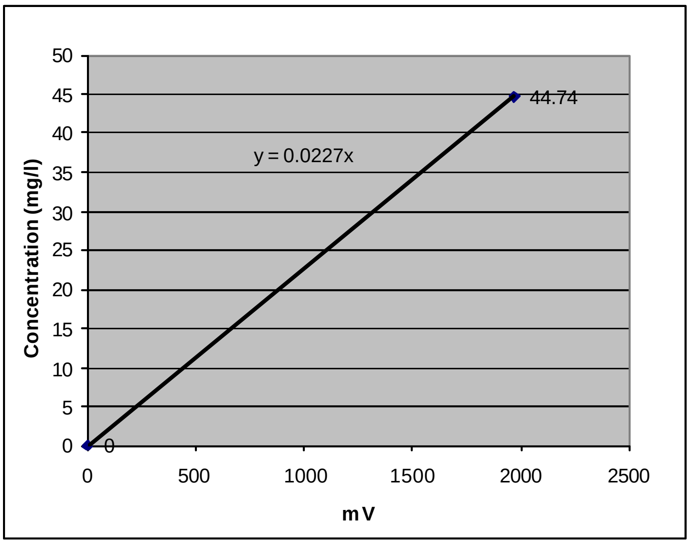


Fig.A3-2. Electrode calibration results for Exp. 1RTN

Fig.A3-3. mV vs Time (min) for Exp. 1RTN

12.3.2. Exp. 2RTN

Oxygen is dissolved in water by means of pure oxygen purging and both oxygen dissolved water and membrane bioreactor are kept at room temperature (18^0C)



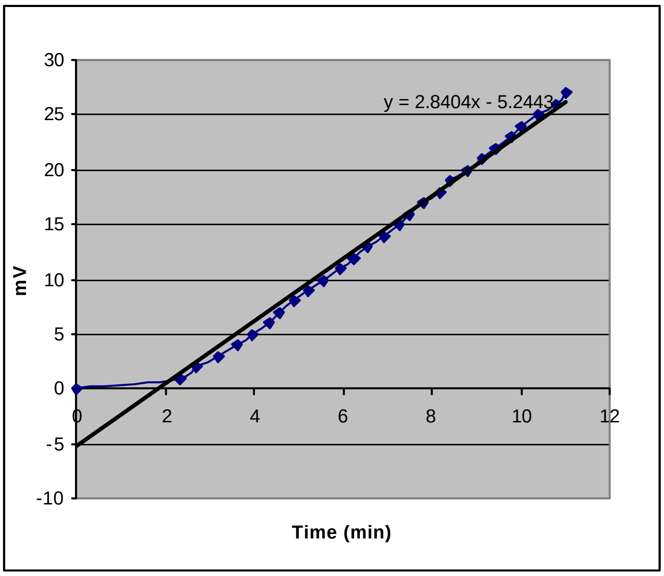


Fig.A3-4. Electrode calibration results for Exp. Exp.2RTN

Fig.A3-5. mV vs Time (min) for Exp.2RTN

13. Appendix B
Determination of pure oxygen solubility at elevated temperatures

The equilibrium concentration of dissolved gas in a liquid is a function of type of gas and the partial pressure of the gas in contact with the liquid. The relationship between the mole fraction of the gas in the atmosphere above the liquid and the mole fraction of the gas in the liquid is given by Henry's law.

$$P_g = H.x_g \qquad (8)$$

Where p_g : Partial pressure of the gas (atm), H : Henry's law constant (atm), Xg : mole fraction of gas in water
The change in the Henry's law constant with temperature can be estimated using the modified form of the Van't Hoff- Arrhenius relationship[1]

$$Log_{10}\, H = -A/T + B \qquad (9)$$

Where H = Henry's law constant at temperature T, in atm

A = empirical constant that takes into account the enthalpy change in water due to the dissolution of a component in water and the universal gas law constant.
T = temperature, K
B = Empirical constant

13.1. Determination of Solubility of pure oxygen at 40°C

Temperature coefficients at 40^0C (Table 2.8, page 67[1]).
A = 595.27 B = 6.644
$Log_{10}H = -A/T + B = -595.27/(273.15 +40) + 6.644 = 4.743$
H = 55335atm
Assuming pure oxygen partial pressure = p_g = 1 atm
$x_g = 1/55335 = 1.8072 \times 10^{-5}$
$n_g /(n_g + n_w) = 1.8072 \times 10^{-5}$
Where n_g = number of oxygen moles in water and n_w = number of water moles
Since 1l water = 55.6 mole and ng + 55.6 = 55.6 mole
$n_g = 100.48 \times 10^{-5}$ mole O_2/l = 32.15 mg/l
Therefore solubility of pure oxygen at 40°C is 32.15 mg/l

13.2. Determination of Solubility of pure oxygen at 21^0C

Temperature coefficients at 21^0C (Table 2.8, page 67[1]).
A = 595.27 B = 6.644
$Log_{10}H = -A/T + B = -595.27/(273.15 +21) + 6.644 = 4.620304$
H = 41716.12atm
Assuming pure oxygen partial pressure = p_g = 1 atm
x_g = 1/41716.12 = 2.3972 x10-5
$n_g /(n_g + n_w) = 2.3972 \times 10^{-5}$
Where n_g = number of oxygen moles in water and n_w = number of water moles
Since 1l water = 55.6 mole and ng + 55.6 = 55.6 mole
n_g = 133.284 x 10-5 mole O_2/l = 42.65 mg/l
Therefore solubility of pure oxygen at 21°C is 42.65 mg/l