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USE OF DISSOLVED OXYGEN CONCENTRATION PROBES IN BIOLOGICAL WASTEWATER TREATMENT PLANTS

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ABSTRACT

A study on use of dissolved oxygen probes (DOP) for measurement of oxygen concentration in water and wastewater treatment is presented. The principles of operation, design considerations and selection criteria for two types of probes, viz. galvanic and polarographic, are discussed. Use of polarographic probes in a three-phase fluidized bed bioreactor and in laboratory experiments is presented and discussed. The effect of air flow rate and treatment time on dissolved oxygen concentration was found to be significant. It was found that polarographic probes are important equipment in determining the pollution of the industrial effluents. Finally, the use of the DOC probes in treatment process was recommended.

INTRODUCTION

The factors that influence the dissolved oxygen concentration (DOC) in wastewater treatment process include, among others, mechanism and rate of aeration, cell concentration and solute or impurities contents in the medium. DOC meters are used in industrial wastewater treatment plants to measure the oxygen available for biological activity. In the receiving wastewaters, DOC meters are used to monitor the DOC in water which is the measure of pollution level of the water.

Among the factors that influence the dissolved oxygen concentration in wastewater treatment bioreactors are: mechanism and rate of aeration (whether sparging, surface aeration or membrane aeration); cell concentration which increases with treatment time; and solute or impurities content of the medium (organic and inorganic).

When organic compound enters a waterway, the dissolved oxygen is consumed during its breakdown by aerobic microorganisms, namely:

$$\{CH_2\} + O_2 \rightarrow CO_2 + H_2O \qquad (1)$$

$$NH_4^+ + 2O_2 \rightarrow 2H^+ + NO_3^- + H_2O \qquad (2)$$

Beside consumption of dissolved oxygen by microorganisms, oxygen is also consumed rapidly by the bio-oxidation of nitrogenous material represented by an ammonium ion, that is

The chemical or biochemical oxidation of chemical reducing agents also consume dissolved oxygen in water. These are mainly ferrous salts and sulfite ions, as shown in equations (3) and (4), respectively. All these processes contribute to the deoxygenation of water. The *BOD* (biological or biochemical oxygen demand) is a measure of oxygen consumption by microbially mediated oxidation of contaminants in water.

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+ \quad (3)$$

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2+} \quad (4)$$

The discharge of industrial effluents into moving or stationery water masses has other detrimental effects to the environment. River banks, ocean beaches and lake shores have been rendered useless due to deposition of oils and odorous substances, while oxygen penetration from the air into water has been made difficult due to oily layer at the surface of water receiving effluent from refinery plants. High chemical oxygen demand of the effluent from brewery industries deplete dissolved oxygen in the receiving water causing production of odorous smells and encouraging eutrophication. The solution to these problems is to treat the industrial wastewater to reduce to minimum the concentration of the pollutants they carry, before discharging into the available water masses. Biological treatment, utilizing a mixed culture of microorganisms remains the most useful form of treatment form of industrial wastewater because it suits many kinds of effluents.

LITERATURE REVIEW

Among various environmental and nutritional factors that influence metabolic activities in an aerobic bioreactor performing carbonaceous removal, oxygen is a critical parameter since it is the only nutrient that has to be provided continuously, even in batch processes [1, 2]. Transport processes in bioreactors are the origin of scale-up problems. The dissolved oxygen concentration is one of the key parameters in large scale plants and is directly dependent on transport processes. Oxygen transfer from a dispersed air phase is important for most microbial reactions, and because of its low solubility, oxygen often becomes the limiting substrate for large reactors [3]. In such cases the dissolved oxygen concentration will be very low throughout the bioreactor, and in some less well-mixed and poorly aerated dead zones it might fall to zero. In several studies, the dissolved oxygen concentration was just not allowed to drop below a certain concentration and no attempts have been made to establish mathematical relation between dissolved oxygen concentration and the kinetics of the wastewater treatment process [2]. The effect of oxygen concentration on its uptake rate by the microorganisms has been shown to increase linearly with the dissolved oxygen concentration up to a critical value, beyond which the oxygen uptake rate remains practically constant [4].

In a bioreactor, aerobic microorganisms depend solely on the oxygen solubility and diffusion coefficients. Thermodynamically, oxygen solubility indicates the maximum capacity of oxygen that can be dissolved in wastewater, the oxygen diffusion on the other hand, is a transport property of the solution which characterizes the degree of easiness of transporting oxygen in the liquid. A reliable and convenient method of measuring simultaneously oxygen diffusion coefficients and solubility using membrane covered oxygen electrode has been presented in work [5]. There, measurements were conducted in electrolytic solutions of sodium chloride, potassium chloride, sodium sulfate, and magnesium sulfate over a wide ranges of concentrations. A method coupling the steady- and unsteady-state analysis for oxygen diffusion through a thin layer of test solution on the surface of a membrane-covered oxygen electrode was used in their study. The method can be used for viscous, non-Newtonian, polyelectrolyte solutions and fermentation media.

The quality of the purified water from a wastewater treatment plant should be maintained constant despite the variations, whether periodic or not, of load and flow rate, of the variability of biomass, made of different species, and the hydrodynamic characteristics of the plant. In carbonaceous removal, large amounts of oxygen should be provided either by gas injection or surface aeration in order to avoid the minimization of the biomass activity. Depending on the aerator type, the dissolved oxygen concentration level in the wastewater treatment vessel and the effluent chemical oxygen demand can be kept high or low. For instance, a novel membrane aeration system will keep the chemical oxygen demand level in the effluent at minimum, and if aeration is switched to ring-sparger aeration, the chemical oxygen demand rises significantly due to a significant drop in aeration efficiency. This is because, membrane aeration maintains higher dissolved oxygen concentration level and on switching the air supply to a ring-sparger the dissolved oxygen concentration falls to zero [6].

In wastewater treatment bioreactors, the oxygen transfer rate can be determined rom the dissolved oxygen concentration measurements. In this case, modeling of data is based on the assumption that the membrane electrode measures only the liquid-phase dissolved oxygen concentration. Several methods have been proposed for determination of the gas-liquid volumetric oxygen transfer coefficient, k_La. While other researchers measure steady-state oxygen concentration in the liquid phase, others employ dynamic methods of unsteady state gas absorption or desorption. From the dissolved oxygen concentration measurements, k_La values can be evaluated either by non-linear curve fitting in the time domain of gas-absorption or by using the slopes of lines obtained from semilogarithmic plots of liquid- or gas-phase solute concentrations. It has been found out that the slope method results into a more reliable and consistent k_La values than the non-linear curve fitting, and also that the former is much less sensitive to the transport lag of oxygen measurements in the liquid phase than the latter [7].

METHODOLOGY

Ouyung et al. [7] determined k_La values by assuming a batch liquid phase, a method which is valid for a wastewater treatment system when the residence time of the liquid-phase is less than one hour. Two bioreactor models, the plug flow and the static continuously stirred tank reactor models, were used to calculate k_La values from the measured dissolved oxygen concentration. The static continuously stirred tank bioreactor model, *CSTR*, led to k_La values denoted as $(k_La)_{CT}$ in this work, as given in equation (5). This model assumes that the mixing is so rigorous that each phase of the bioreactor contents is of uniform composition, i.e. concentrations of oxygen in any phase do not vary with position inside the bioreactor. Because of complete mixing, the dissolved oxygen concentration is the same throughout the bulk liquid phase. This model is emphasized by the presence of solids which break gas bubbles and move randomly as a result of the kinetic energy absorbed from the air bubbles emerging from the distributor holes.

$$(k_La)_{CT} = \frac{u_L}{\Delta Z}\left(\frac{C_2 - C_1}{C_g{}^* - C_2}\right) \tag{5}$$

The plug flow bioreactor model, *PFR*, assumes that the phases move axially without lateral mixing. The mass balance can be formulated on the column using the differential-section approach. The basic steady-state conservation equation is applied to a thin slice of the bioreactor taken perpendicular to the vertical axis. This model led to k_La values denoted as $(k_La)_{PF}$, equation (6).

$$(k_L a)_{PF} = \frac{u_L}{\Delta Z} \ln\left(\frac{C_2 - C_1}{C_g^* - C_1}\right) \tag{6}$$

The increase in use of dissolved oxygen concentration probes has developed after the introduction of scientific and engineering background into its basics and theories. Particularly, the use of the probes in wastewater treatment plants has stimulated a growing interest in their fundamental properties and operating principles. The diverse aspects of the use of the probes have been discussed in a number of papers and reviews, as shown in *Table 1*, to mention a few. It can be seen from *Table 1* that oxygen probes has been in use since the 1950's in other fields of engineering, while the use of probes in wastewater treatment came into being very late.

Table 1 List of reviews and systematic treatment of oxygen probes theory and practice [1]

Davies(1962), Brown (1970)	Review of oxygen probes applications for long term experiments in microbiology, summary of biological applications
Fatt (1976)	Detailed account of construction and of application of probes in biology, medicine and technology
Lee and Tsao (1979)	Review of probe construction, general design considerations, oxygen probe applications in various fields and sources of measurement errors due to probe characteristics
Gnaiger and Forstner (1983)	Use of oxygen probes in medicine, physiology, biotechnology and environmental science

The diversity in the behavior of real oxygen probes stems from the variety of combinations of several basic construction elements and design concepts. Among the factors considered during the probe selection were: probe type (polarographic or galvanic); electrode metals (anode and cathode); electrolyte solution, and membrane material, the details of which are given under design considerations.

While modeling the liquid-phase chemical reaction and interphase mass transfer in churn turbulent bubble columns [8], examined the behavior of the slug and cell model in the presence of interphase oxygen transfer in water, when there is no liquid-phase chemical reaction taking place. Using dissolved oxygen concentration measurements, it was possible to compare the slug and cell model simulations with the experimental data from the steady state dissolved oxygen concentration measurements along the column length. A comparison between slug and cell model and the axial dispersion model with the experimental data for the absorption of oxygen in water revealed a good agreement.

Tang *et al.*, (1987) [9], studied the degradation of phenol in the draft tube three-phase fluidized bed bioreactor by determining the amount of oxygen per gram of phenol consumed. In their work, the analysis of the off-gas composition was performed using the *Beckman Model 755* oxygen gas analyzer while the dissolved oxygen concentration in the liquid was measured using a *YSI Model 54ARC* dissolved oxygen concentration meter and probe, inserted at the top of the liquid surface. The k_La was determined using the method that involves dissolution of benzoic acid.

Dissolved oxygen concentration meters have also been used while determining the volume referred mass transfer coefficient, k_La, in agitated vessels of standard configurations [10]. The oxygen mass transfer rate into an aqueous slurry were determined by the dynamic method after deoxygenating the slurry by sparging with nitrogen. After starting the air flow and agitation, the transient dissolved oxygen concentration in the slurry was measured with a fast response polarographic probe, model *WTW EO 90,* at a mean temperature of 25°C. The air flow rate range was from 20 to 250 liter per hour with the solids loading up to 10% by volume. The same type of probe was used by Schumpe *et al.*, (1987) [11], for determining the k_La in the suspensions of kieselguhr (7 mm), aluminium oxide, (8 mm), and activated carbon (5 mm), in water and 0.8 molar solution sodium sulfate solution.

Fan *et al.*, (1987) [12], used dissolved oxygen concentration probes to study the gas-liquid mass transfer characteristics in a two-stage draft-tube gas-liquid solid fluidized bed (*DTFB*). The dissolved oxygen concentration was measured at the top of each stage using a polarographic probe *Models 5750* and *5739*. While the bottom probe was mounted horizontally, the top probe was held vertically. In their study, dissolved oxygen concentration measurements were modeled to give k_La values for each stage as well as the overall configuration k_La values. The dissolved oxygen concentration at the bioreactor inlet was taken to be zero due to a complete reduction of dissolved oxygen by sodium sulfite.

Industrial wastewater is a combination of different organic and inorganic compounds, having different effects on dissolved oxygen concentration. A measured value is normally a resultant of the effects of these components. In this work, effects of solute concentration on dissolved oxygen concentration in distilled water was measured separately for the following compounds: sodium chloride, ammonium sulfate, phenol and acetone. The sodium chloride and ammonium sulfate were selected mainly because they are among the salts comprising the nutrients added to the bioreactor during growth of microorganisms.

This paper outlines the importance of dissolved oxygen meters, theoretical background, principles of operation and design features. Further, the paper discusses the experimental data on effect of selected compounds on dissolved oxygen concentration. The oxygen transfer rate in water and industrial wastewater in a three-phase fluidized bed bioreactor utilizing a novel biomass support, the KMT^R was modeled from the dissolved oxygen concentration measurements.

The problems caused by industrial effluents discharged into water are of wide range. When water containing organic compounds is discharged into a river, lake or an ocean, microorganisms grow and multiply very faster in the receiving water due to high availability of nutrients. The microorganisms feed on the compounds (substrate) and respire using naturally dissolved oxygen (that is, oxidation in organic matter). Thus, when an organic compound enters a waterway, dissolved oxygen is consumed during its breakdown by aerobic microorganisms. The compounds are then said to exert a demand on the availability of dissolved oxygen. If the dissolved oxygen is used up faster than the rate at which it can be replaced, the water becomes deoxygenated, and neither *flora* nor *fauna* can survive in the water. Unless the water is reaerated efficiently, as by turbulent flow in a shallow stream, it rapidly becomes depleted in oxygen and will not support higher forms of aquatic life. The oxygen demand exerted by an organic substance is thus a measure of its power to cause water pollution, and pollution results when the oxygen demand exceeds the availability of oxygen.

PRINCIPLES OF OPERATION

Dissolved oxygen meters consist of an electrochemical cell, the probe and a signal conditioner or a transmitter. The two principal types of electrochemical cells used in dissolved oxygen probes are the galvanic and the polarographic cells. Galvanic and polarographic cells have very similar operating principles, both consisting of an electrolyte and two electrodes as shown in *Fig. 1*. The polarographic cell requires a polarizing voltage in the range of 0.5 to 1.0 V direct current. In one proprietary probe design, the electrodes are immersed directly in the process stream where process fluid acts as the electrolyte. However in most commercially available probes, the electrolyte is obtained by a gas permeable membrane, and oxygen is brought into contact with the electrodes by the action of diffusion. When an electrode of noble metal such as platinum or gold is made 0.5 to 1.0 V negative with respect to a suitable reference electrode, for example calomel or silver-silver chloride combination, in neutral potassium chloride solution, dissolved oxygen is reduced at the cathode surface. Whether the probe is of the membrane or non-membrane type, oxygen is reduced at the cathode and at the anode, the anode metal is oxidized. The overall electrode reactions are as follows:

At the cathode:

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \qquad (7)$$

$$H_2O_2 + 2e^- \rightarrow 2OH^- \qquad (8)$$

At the anode:

$$Ag + Cl^- \rightarrow AgCl + e^- \qquad (9)$$

The result of this oxidation/reduction process is a flow of electrons (current) from the cathode to the anode proportional to the oxygen dissolved in the process stream. The meter readings are then obtained from this current. The rate of the oxidation/reduction process is strongly affected by the temperature. Therefore, accurate temperature measurement and compensation is essential for accurate dissolved oxygen concentration measurements. Temperature is usually monitored by a transmitter located in the probe, as shown in *Fig. 1*, and compensation is made in the signal conditioner/transmitter electronics. By separating the cathode, anode and the electrolyte from the test medium with a plastic membrane permeable to oxygen but not to ions, the polarographic oxygen electrode has been successfully employed to measure the oxygen partial pressure in the liquid, gas or semisolid. With proper interpretation, the measurements can be used to characterize the transport properties of oxygen in the bulk medium surrounding the electrode [5].

Suspended and dissolved substances in the process stream can also affect the electron flow. When solids accumulate on the membrane, they reduce the rate of oxygen transfer to the electrodes. In one design, a mechanical grindstone continuously polishes the surface of a membrane probe to keep the electrodes clean. To maintain gas permeability, fouled membrane probes must be manually cleaned. Certain dissolved gases interfere with the dissolved oxygen concentration measurements by either non-membrane or membrane probes. Common gas to be avoided are chlorine, hydrogen sulfide, carbon dioxide and sulfur dioxide. While chlorine will be read by the probe as oxygen, carbon dioxide can neutralize some electrolytes. On the other hand, hydrogen sulfide and sulfur dioxide can poison some metals used for an anode. The combined dissolved oxygen concentration measurement accuracy of ±1 to ±4% of full scale can be achieved in most meters under the conditions generally encountered at wastewater treatment plants. For a meter with range 0 - 20 mg/l dissolved oxygen (as the one used in this work) the uncertainty was 0.8 to 1.6 mg/l.

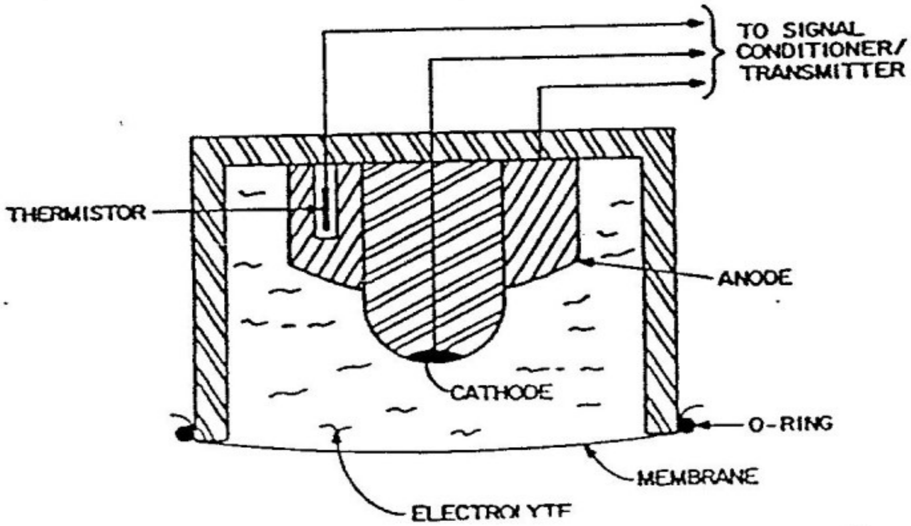

Fig. 1 Membrane type dissolved oxygen concentration probe

It is advantageous to confine the main resistance to oxygen transfer within the membrane, where the resistance is well defined. Thus, the membrane not only prevents contamination of the electrode surfaces, but also ensures reproducible oxygen transport to the cathode. It is however, unwise to increase membrane resistance up to values at which the resistance of the liquid film becomes insignificant, since then the probe response is usually too slow [1]. Therefore, the liquid film resistance should generally be taken into account. A chemical reaction with dissolved oxygen occurring in the bulk of liquid, and thus also in the liquid film before the membrane, will affect oxygen transport through the film and, consequently, the probe reading. When the chemical reaction is rapid enough, all of the transferred oxygen may be consumed within the film so that the probe reading is zero, even if the dissolved oxygen concentration in the bulk liquid is quite high. Studies on situations involving a chemical reaction are, however, rather scanty.

The theory of oxygen transport to the probe cathode involves two groups of models: the steady-state and unsteady-state models. The steady state analysis assumes that: the gas film resistance is negligible; liquid at the gas-liquid interface is saturated with oxygen in the gas phase, regarded as the source of oxygen diffusion; the rate of oxygen consumption due to the reaction at the cathode is much faster than the rate of diffusion so that the partial pressure of oxygen at the cathode surface is nil; resistance of oxygen transfer in the electrode solution is negligible especially when the membrane is attached to the cathode surface, and that the oxygen transfer in a membrane covered electrode is controlled by the oxygen diffusion through the membrane. The unsteady-state model considers the oxygen diffusion through a thin liquid film on the membrane-covered electrode to be a bi-layer system, that is the test solution and the membrane, while neglecting the resistance of oxygen diffusion in the electrode solution. Bi-layer models have been developed primarily for the estimation of the sensitivity of the oxygen concentration probes to the hydrodynamics of the external fluid phase (flow velocity), in which case, the liquid film resistance to oxygen transport has to be considered in addition to that of the membrane layer. However, the analysis for the unsteady state diffusion in a composite bi-layer remains complicated. For the two layer model, the underlying assumption are: oxygen flux to the electrode is negligible, restricting the analysis to the liquid layer only; the thickness of the liquid layer is taken to be very large compared to the membrane thickness (about one-hundred times for teflon membrane), so that there exists a linear profile of oxygen partial pressure within the membrane [1, 5]. Assumptions underlying all the models can be listed as follows: that, only the normal component of the oxygen flux towards the cathode is significant; permeability, diffusivity, and thickness of each layer are constant; ant that the electrode reactions proceed in the limiting diffusion current (at which a polarogram, which is a plot of electrode current against voltage, shows a plateau) [1].

PROBE DESIGN CONSIDERATIONS

The factors considered during selection of the probe were: type electrode metals, type electrolyte, membrane material and whether to use a galvanic or a polarographic electrode. The details of each of the factors are given below.

Platinium, gold and silver are the most frequently used cathode metals. Platinium cathodes stick well on glass but unlike silver and gold, shows aging effects and like silver, are very susceptible to hydrogen sulfide poisoning. Platinium cathodes have to be polished, their performances may vary depending on their fabricating history and in an acidic medium the reaction on the platinium surface may not procced at a sufficient rate. Gold cathodes are resistant to hydrogen sulfide poisoning. Unlike platinium, the electrode reactions on gold and silver are free from interfering effects of surface oxides. Gold purity governs the width of the current-voltage plateau, as well as the magnitude of residual current. In this work, a probe with *gold* cathode was selected. Silver/silver-chloride, silver/silver-oxide and calomel electrodes are most frequently used as anode. Silver oxide may flake off the anode and short circuit the probe, a problem not encountered with silver-chloride. Thus a *silver/silver-chloride* anode was selected. The anode was large enough to avoid polarization.

Available options for electrolytes are solid electrolytes and aqueous salt solutions. The salt solutions are the most commonly used and they include: saturated potassium chloride, potassium hydroxide, and buffered solutions of sodium carbonate, sodium phosphate and the acetate buffer. Saturated solution of potassium chloride causes undesirable deposition of silver on the cathode, increasing the residual current, except when a 0.75 kmol/m^3 is used. Potassium hydroxide in which substitution of chloride for hydroxide ions does not take place, causes silver oxide to flake off the anode. Buffered solutions which prevent changes in pH are recommended in the presence of carbon dioxide. In this work, a *0.75 kmol/m^3 potassium chloride* solution was used as an electrolyte. The latter was included in the dissolved oxygen concentration meter accessories in 250-ml ampoules.

For the membrane, the most important properties are the solubility and diffusion of oxygen, water and other gases in the membrane material. *Table 2* gives the physical properties of membrane materials. The *PTFE membrane* was selected because of the following reasons: it offers high heat resistance and it is mechanically strong, thus resistant to structural changes; *PTFE* cannot be hydrated, its oxygen solubility and diffusivity remains constant, compared to polyvinyl fluoride and polyvinyl chloride membranes whose permeability increases several times in presence of water. Despite that the inelastic *PTFE* cracks when stretched, it has the advantage of high resistance and extremely low water permeability. The parameters of polyethylene and propylene are not stable over the long term, but they have conveniently low oxygen permeability.

Natural and silicone rubber membranes squeeze out electrolyte from the space between the membrane and the cathode.

Table 2 Physical properties of membrane materials [1]

Material	Maximum temperature	Oxygen		Water	
	°C	$k_M \times 10^{16a}$	T, °C	$k_M \times 10^{16}$	T, °C
Polytetrafluoroethylene *(PTFE)*	230	29.2 26.2	20 30	28.4	38
Polyethylene, *(HD-PE)^b(LD-PE)^c*	80	12.4 21.4	30 30	187 190	25 25
Polypropylene *(PP)*	130	12.4 5.0	30 20	159	25
Polystyrene *(PS)*	80	10.4	30	2180	25
Polyvinyl chloride *(PVC)*	50	2.86	20	940	25
Silicone rubber *(SR)*	-	286	30	61400	25

$k_M \times 10^{16a}$ = mol/m.Pa.s, measured in aqueous-aqueous phase
HD-PE^b = high density polyethylene; *LD-PE^c* = Low density polyethylene

While galvanic probes use an electrode pair (silver cathode and lead anode) that generates a potential to ionize oxygen and thus requiring no external voltage source, polarographic probes require an external battery. A polarographic probe with silver anode was selected because it has constant linearity and stability. A probe is said to be linear when its sensitivity does not depend on the oxygen tension, and all oxygen probes applications require linear probes. Instability means a change in sensitivity with time which may occur at various rates over the time scale of measurement. An initially linear probe may begin, for various reasons, to show non-linear behavior. For example, the oxygen reduction rate at a platnum cathode may decrease with time; excessive oxygen chemisorption in the surface of the oxide layer may, like other adsorbed gases or impurities, prevent adsorption and thus also reduction of oxygen; or conversely, the oxide layer may not be so developed as to catalyze peroxide decomposition at a sufficient rate. These situations do not arise at a sufficiently negative potential provided by an external battery, making polarographic probes more prominent.

While thinking of purchasing dissolved oxygen meter, one have to consider different manufacturers' options and select the suitable design that suits the applications in hand. New designs include remote calibration units that can be installed near the probe to permit calibration where the transmitter is not within 50 ft or is not located within sight of the probe. The meter reading range affects the accuracy of the instrument and should be selected wisely. The common ranges are: 0 - 5, 0 - 10, 0 - 20 and 0 - 40 mg/l. The transmitter output signals are also variable, for instance: 0 - 5 V, 4 - 20 mA, or 10 - 50 mA direct current. The meter input power is another factor which must be considered prior to selecting a dissolved oxygen meter, as this must match with the available a.c/d.c adapters. Probe cable-length should be selected to fit the requirements in the treatment plant. Data acquisition from a meter provided with an *RS* output connection becomes simple when a meter is connected to a computer.

EXPERIMENTAL WORK

Experiments were conducted on the bioreactor column as well as in laboratory vessels.

(a) Bioreactor column

The total capacity of the bioreactor used for measurements of dissolved oxygen concentration in water and wastewater was approximately 70 liter. Dilution of wastewater samples, pH regulation and addition of nutrients was performed in the feed tank. Mixing was effected by fluidization and recirculation of liquid between feed tank and the column, *Fig. 2*. The dissolved oxygen concentration was measured by using two probes directly inserted into the column at a distance of 1.70 m apart, the bottom probe being 10 cm above the distributor plate. At regular time intervals, 150 - 200 ml sample was withdrawn for analysis. One part was used for dry weight analysis, the second sample was used for chemical oxygen demand *(COD)* measurements using a photometer.

Dissolved oxygen concentration values at any other level between the two probes were measured using a third probe which was lowered into the column to the desired level, using the 2-m long probe cable. The dissolved oxygen concentrations were measured at different air velocities, u_g, and at different dilution ratio, R_v (volume of wastewater sample to volume of tap water). Two wastewater samples were used in this work, that is, wastewater from Tanzania Breweries Limited (denoted as *TBL*) and wastewater from Tanzania-Italy Petroleum Refinery Company (denoted as *TIPER*). The bioreactor operational parameters considered include: dilution rate, *Rv*; treatment time; air velocity and elevation along bioreactor column, *Z*. Details of the experimental rig are given in Fig. 2.

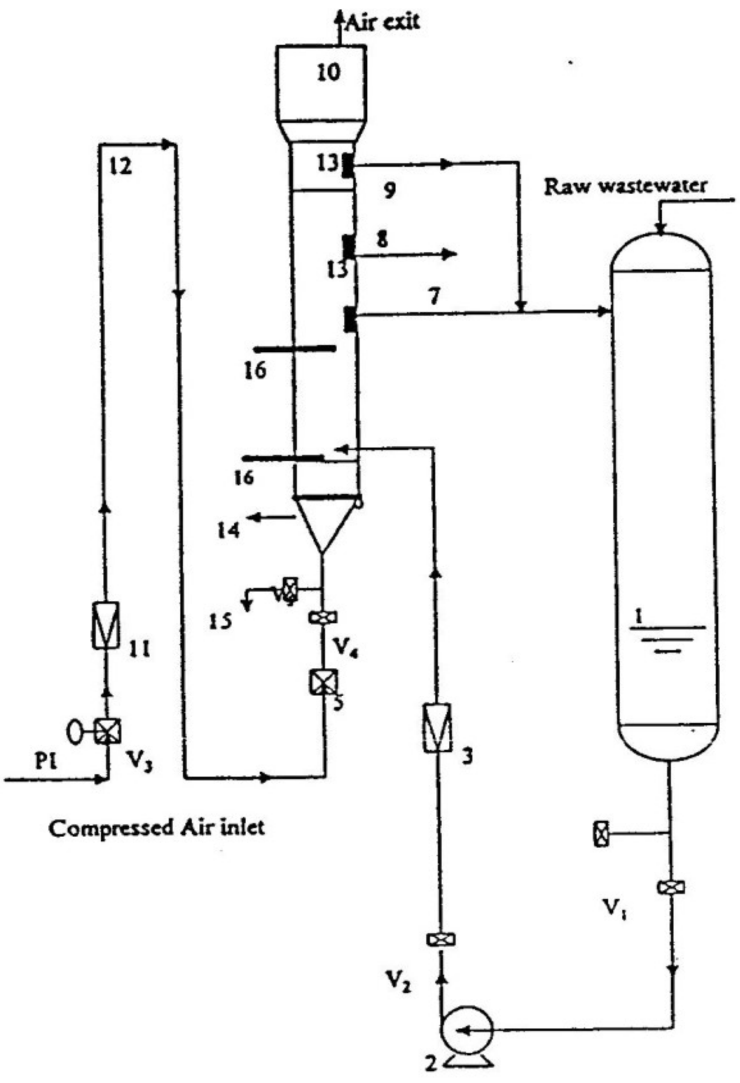

Fig. 2 Schematic diagram of the experimental rig

KEY: *1* - Feed tank; 2 - Centrifugal pump; *3* - Liquid rotameter; *4* - fluidization column; *5* - Non-return valve; *6* - Distributor plate; *7,9* - Liquid recirculation branch; *10* - Foam breaker tank; *11* - Gas rotameter; *12* - Compressed air inlet; *13* - particle carryover prevention sieves; *14* - Sampling point; *15* - Liquid discharge line; *16* - Dissolved oxygen concentration probes; *V* - Valves; *PI* - Pressure indicator and valve.

(b) Laboratory experiments

The effect of different compounds on dissolved oxygen concentration was examined in a 1000-ml beaker containing distilled water. A magnetic stirrer was used to effect mixing of the beaker contents. Tested compounds were: ionic salts (sodium chloride and ammonium sulfate); organic compounds (acetone and phenol). Effect of temperature on dissolved oxygen concentration was also measured by adding ice in hot water at 40°C until the temperature reaches 8°C. The experiment was repeated by heating the contents of the beaker from 8°C to 40°C. The maximum temperature of 40°C was not exceeded as per manufactures recommendations. Three probes were inserted into the same beaker to read dissolved oxygen concentration values, results of which are presented in *Fig. 8* and *9*.

RESULTS AND DISCUSSION

It was observed that treatment of wastewater samples proceed at a constant dissolved oxygen concentration after one day up to sixth day. The minimum dissolved oxygen concentration was found to be 8 mg/l and 4 mg/l for *TBL* and *TIPER* wastewater samples, respectively, as shown in *Fig. 3*. Thus, a precise mechanism of oxygen control is required using the above values as set points. It has been recommended by Linek *et al.*, (1985) [1], that dissolved oxygen concentration should be controlled using a proportional integral derivative *(PID)* controller applied to the mass flow system, adding pure oxygen and nitrogen to the constant air flow. The decrease in dissolved oxygen concentration within the first day was attributed to the period of microbial growth. It can be seen from *Fig. 3* that, treatment of *TBL* samples proceeded at higher level of dissolved oxygen concentration than *TIPER* samples, due the latter being heavily contaminated with aromatic hydrocarbons.

The decrease in dissolved oxygen concentration during the first day was accompanied by the sharp decrease in *COD* during the first day, followed by a slow decrease in *COD* for the rest of the days, as shown in *Fig. 4*. From *Fig. 4*, it can be seen that at higher air flow rates, the *COD* removal was faster. This was partly due to increased mixing in the bed and partly due to sufficient supply of oxygen.

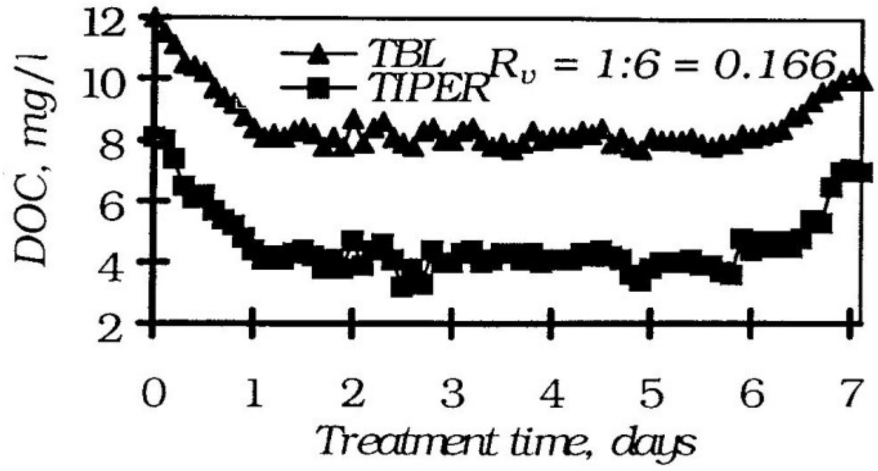

Fig. 3 DOC values in treatment of brewery and refinery wastewaters in a three-phase fluidized bed bioreactor

(at room temperatureof of 27°C, air velocity $u_g = 25$ mm/s, liquid recirculation velocity $u_L = 4$ mm/s, height of the fluidised bed $H_c = 1.88$ m and solid mass $M_s = 2.0$ kg.)

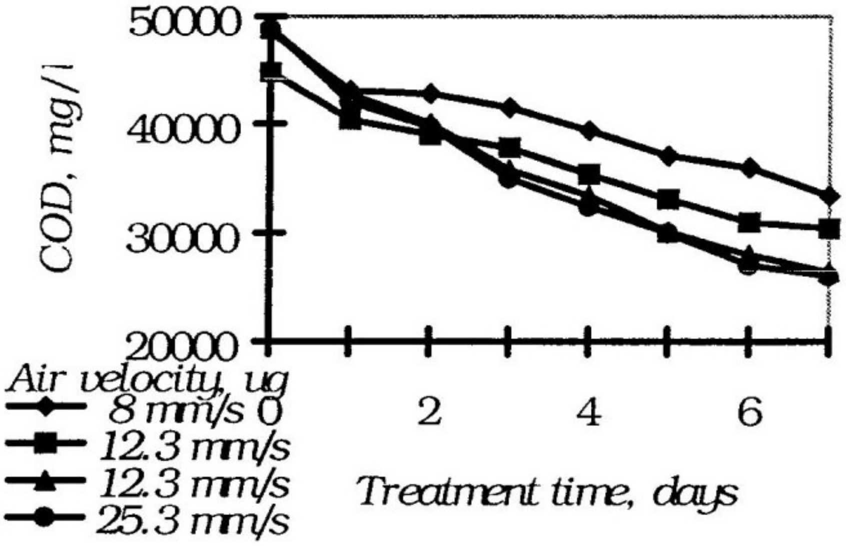

Fig. 4 Variation of *COD* of *TIPER* wastewater samples in the three-phase fluidized bed bioreactor (under similar conditions of *Fig. 3* for three different air flow rates at $R_v = 0.166$.)

The top probe dissolved oxygen concentration was found to increase with the gas superficial velocity, u_g, as shown in *Fig. 5.* The increase in dissolved oxygen concentration with air flow rate reveals that treatment of wastewater at higher air flow rate is advantageous, although this is limited by operating costs. It shows that there was an oxygen transfer from gas- to liquid-phase as the two were rising upwards. Both C_1 and C_2 increased with air flow rate, and C_1 was lower than C_2 at all operating conditions.

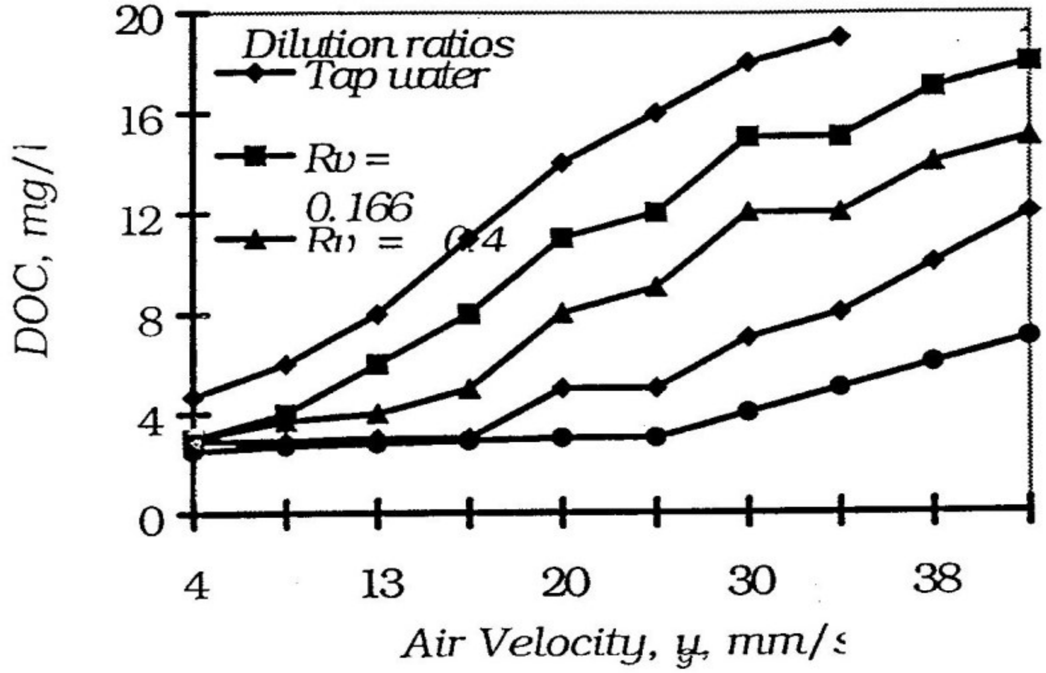

Fig. 5 Values of dissolved oxygen concentration at different air flow rates (for increasing values of dilution rate R_v, values given are average readings of the top probe C_2

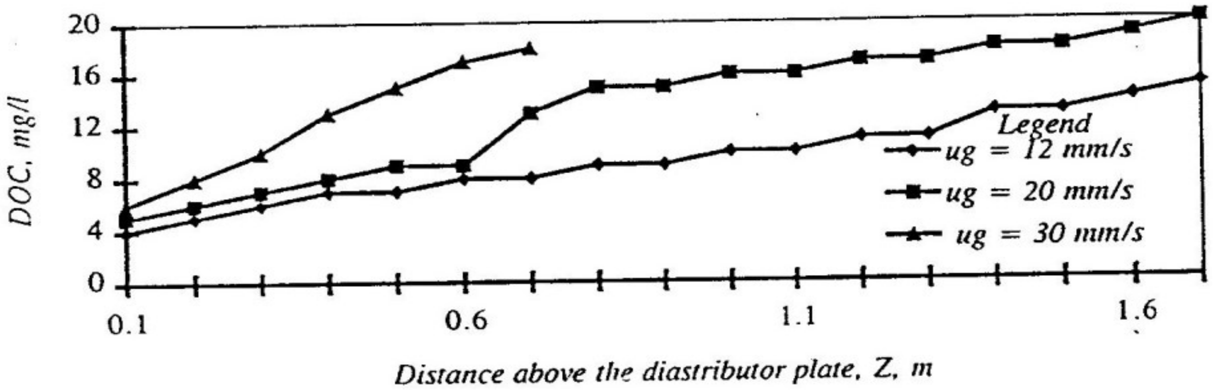

Fig. 6 Values of dissolved oxygen concentration (at different elevations in the bioreaactor, Z, between the probes. The effect of air flow rate is also indicated.)

When dissolved oxygen concentration was measured at different elevations and at different air flow rates in the column, it was found that its value was increasing from the bottom to the top of the liquid level, as shown in *Fig. 6*. At higher air flow rates, for instance 30 mm/s, the dissolved oxygen concentration exceeded the maximum probe reading of 20 mg/l even at a low elevation of 0.6 m. With low air flow rates, dissolved oxygen concentration increased slowly up to 1.7 m. This shows that oxygen dissolution proceeded as the liquid gas rises from bottom to the top.

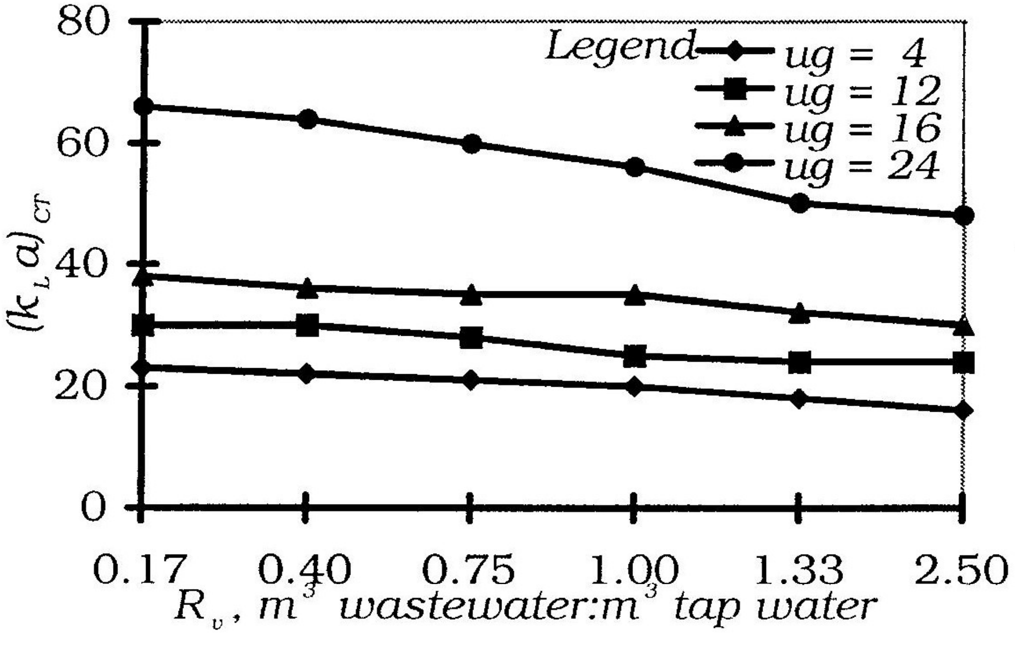

Fig. 7 Variation of the volumetric oxygen transfer coefficient, $(k_L a)_{CT}$, with dilution ratio at various air flow rates. Data collected for *TBL* samples.

In Fig. 7 , the variation of oxygen transfer rate in the three-phase fluidized bed bioreactor with the wastewater dilution rate is presented. A decrease in $k_L a$ as the wastewater volume was increased from 10 liter to 60 liter (that is R_v values from 0.166 to 2.5) was observed at a fixed total bioreactor volume of 70 liter. The same trend was observed at all air flow rates, the effect of R_v being more pronounced at low air flow rates.

Experimental values of dissolved oxygen concentration at varying concentrations of different compounds is shown in *Fig. 8*. While sodium chloride and phenol lowered the dissolved oxygen concentration in water, acetone and ammonium sulfate the later at low concentration) increased the dissolved oxygen concentration. It was important to test the effect of sodium chloride and ammonium sulfate since they constitute a big part of the nutrients added to the medium during treatment of wastewater. The effect of chloride ion on dissolved oxygen concentration compares well with report by Foster and Wase, (1985) [13].

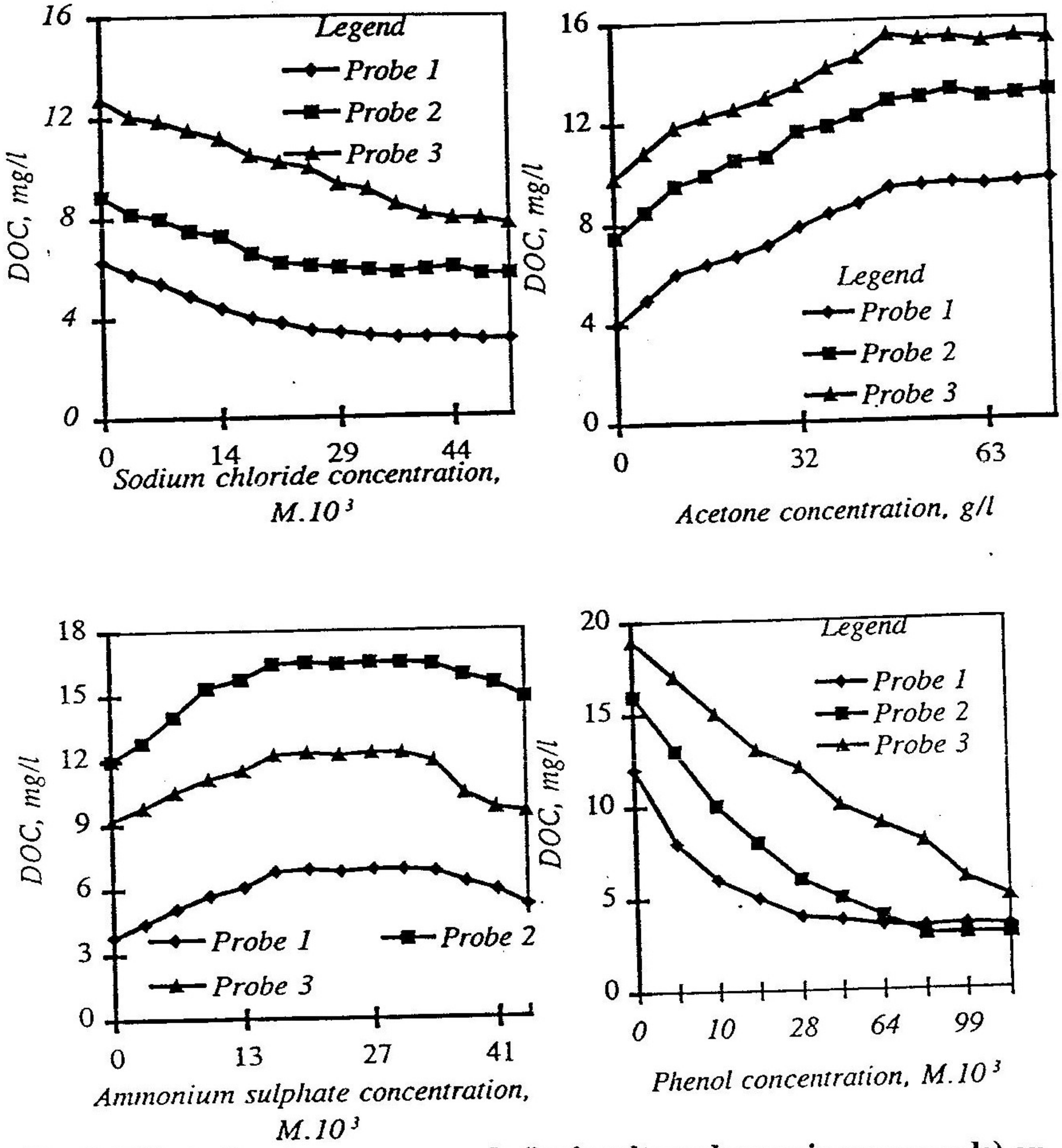

Fig. 8 Effect of various compounds (ionic salts and organic compounds) on dissolved oxygen concentration when dissolved in distilled water at various concentrations.

The effect of phenol on oxygen concentration was studied due to the report that phenol has been recognized to be a nuisance compound in treatment of petroleum effluents as well as surface waters [14]. *Fig. 8* shows how phenol concentration affected the dissolved oxygen concentration in water. It can be seen that dissolved oxygen concentration decreased as the phenol concentration was increasing. Beyond 0.12M phenol concentration, the *DOC* remained practically constant. The decrease in *DOC* was attributed to the effect of impurities on the probe efficiency and also due to the fact that presence of phenol raises the pH of distilled water to about 8.0 (*pKa* value of phenol is 10). Raising the *pH* of the liquid surrounding the cathode requires that the probe polarizing voltage be high [1]. Thus low readings were obtained because the polarizing voltage was fixed at 950 for the probe *Model RL 425*.

The effect of temperature on *DOC* is depicted in *Fig. 9*. The *DOC* was found to decrease as temperature was raised from 8°C to 40°C, and similarly, *DOC* increased as the temperature was decreased in the same range. This shows that low temperature favors dissolution of oxygen. It shows that room temperature was sufficient for operation of the bioreactor. The results agrees well with literature report by Foster and Wase, (1985); Winkler, (1981) [13, 15].

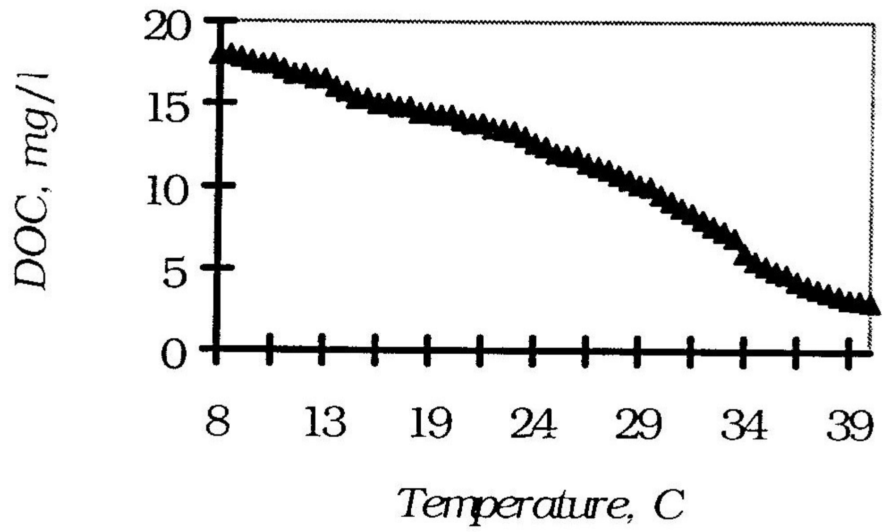

Fig. 9 Effect of temperature on dissolved oxygen concentration

CONCLUSIONS

For oxygen concentration control, the set points for treatment of *TBL* should be 8mg/l and 4 mg/l for *TIPER*; proportional integral derivative *(PID)* controlled mass flow system, adding pure oxygen and nitrogen to the constant gas flow keeping the gas flow constant.

Use of dissolved oxygen concentration meters is only recommended for aeration tanks, oxygenation basins, mixed liquor streams, secondary effluents, plant effluents and sample systems. They are not recommended for use in chlorine contact tanks and hydrogen sulfide bearing streams, as they might interfere dissolved oxygen concentration measurements.

The average *DOC* for treatment time was found to depend on the nature of wastewater. The *DOC* was found to increase with air flow rate and elevation above the distributor plate in the bioreactor column, while it decreased with increasing wastewater volume during dilution.

Sodium chloride and phenol concentration lowered the *DOC* in water, while acetone and low concentration of ammonium sulfate improved the *DOC* in water.

The *DOC* probes are useful instrument in determining the pollution level of water and their use is encouraged in industries and in wastewater treatment plants.

Since *DOC* decreases with increasing temperature, then, thermal pollution will lower *DOC* in the receiving water. It is recommended that the industrial effluents must be left to cool before discharging to the water mass.

Polarographic probes with reading range of 0 - 40 mg/l are recommended to minimize experimental errors.

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NOMENCLATURE

C - dissolved oxygen concentration in bulk liquid, mg/l

C_g* - saturation oxygen concentration, mg/l

H_c - fluidized bed height, m
k_La - volumetric oxygen mass transfer coefficient, h^{-1}
M_s - mass of support charged into bioreactor, kg
R_v - wastewater dilution ratio, m^3 wastewater/m^3 tap water
u_g - air velocity, mm/s
u_L - liquid velocity, mm/s
Z - elevation along the column axix from the distributor plate, m