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OXYGEN TRANSFER RATE IN THE THREE-PHASE FLUIDIZED BED BIOREACTOR WITH KMT^R BIOMASS SUPPORT WHEN USED IN INDUSTRIAL WASTEWATER TREATMENT:

PART I: EFFECT OF AIR FLOW RATE

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ABSTRACT

The influence of air flow rate on oxygen transfer in a three-phase fluidised bed bioreactor utilising novel biomass support, the KMT^R, in industrial wastewater treatment has been extensively studied. The oxygen transfer rate has been expressed in the form of a volumetric oxygen transfer coefficient, k_La. The CSTR and PFR bioreactor models have been applied to evaluate the k_La values from experimental values of dissolved oxygen concentration, leading to k_La values denoted as $(k_La)_{CT}$ and $(k_La)_{PF}$. The kLa values predicted from the hydrodynamic parameters of the three-phase fluidized bed were denoted as $(k_La)_h$. Experimental results have revealed a greater dependency of the k_La values on air flow rate. A greater discrepancy has been observed between k_La values from dissolved oxygen concentration measurements and those predicted from the hydrodynamic parameters of the three-phase fluidised bed. The influence of air flow rate has been examined at different operating conditions of the bioreactor and for different industrial wastewater samples. Experimental results from different models were compared. The k_La values reached a maximum value of 120 h^{-1} for air velocities ranging up to a maximum of 42.5 mm/s. It has been concluded that the k_La values obtained in such a bioreactor configuration are high enough to promote aerobic conditions in the bioreactor, and that the KMT^R support should be used in industrial wastewater treatment.

INTRODUCTION

Various aspects of three-phase fluidization have been the subject of numerous investigations due to its high potential for industrial applications. Three-phase reactors have found prominent use in areas such as industrial wastewater treatment, hydrocracking of petroleum products (like production of ethylene and propylene from vapours of naphtha, steam, air and sand [1]) and fermentation processes. The use of the three-phase fluidized bed bioreactor in industrial wastewater treatment is more advantageous over the other methods because it offers high purification efficiencies, is easy to install and maintain and requires small space, compared to aerated lagoons and waste stabilisation ponds.

The transfer of oxygen from the atmosphere to the micro-organisms within the bioreactor takes a major fraction of the energy budget for the wastewater treatment works [2]. Due to low solubility of oxygen in water and much lower in the wastewater, the aerobic treatment process require continuous aeration to maintain high concentration of dissolved oxygen in the bioreactor, which requires large amount of energy. The transfer of oxygen from the bulk gas (air bubble) to the biofilm, takes a series of steps, the slowest of which is the transfer from the gas film to the liquid film.

In the three-phase fluidized bed bioreactor, air containing oxygen is contacted with wastewater containing a little dissolved oxygen. Thus, there exists an oxygen concentration gradient across the films. The oxygen transfer rate across the interface depends on the driving force and resistance at the respective transfer points. The existence of an interface between gas and liquid-films results in transfer-resistance layers. As air bubbles enter the liquid phase, oxygen molecules are transferred by diffusion into the liquid, until its concentration is the same in each phase, at which stage a dynamic equilibrium is said to exist between the gas and liquid phases, at the expense of oxygen in the air bubble. Under such conditions the rate of oxygen movement from gas to liquid phase and vice versa becomes equal. In actual fact, it is the inequality of chemical potential not the concentration which causes the net transfer of oxygen between liquid and gas phase [3]. When more oxygen is injected into a system at equilibrium, another set of equilibrium will be established, at higher concentrations of oxygen in each phase. In aerobic bioreactors, the equilibrium sites are renewed by introducing new air bubbles to replace the exhausted ones, achieved by

continuous aeration [4].

The fact that air bubbles rise to the surface of the liquid while the oxygen transport is in progress is advantageous because they create space for new bubbles rich in oxygen [5]. The relative velocity between the liquid and the air bubbles is important because of two opposing effects: first, that the more slowly the bubble rises, the longer the time it will be in contact with the wastewater of specific depth before it reaches the surface; secondly, that the faster the bubble rises, the greater the turbulence of the system. Literature reveals that the second factor dominates. The percentage of oxygen transferred from a rising bubble into wastewater during its rise, called the oxygen utilisation efficiency, E_o, as defined by Winkler, (1981) [5], in the following equation:

$$Eo = (1 - \frac{n_2}{n_1}) \times 100\% \qquad (1)$$

where n_1, n_2 are the initial and final number of moles of oxygen in the gas bubble.

Winkler reported that E_o is higher at small bubble diameters, the latter being proportional to the air flow rate and liquid height above the distributor plate. Thus using a distributor with fine holes increases the oxygen transfer rate. High liquid viscosity has been reported to reduce the bubble rising velocity causing a strong aggregation of bubbles at the bottom of the column, leading to concentrated coalescence [5]. Air flow rate affects the bubbles characteristics, studies of which can be easily understood by analysing the relationship between bubble size and velocity of a single bubble. The study made by de Lassa *et al.*, (1986), reports that this relationship is affected again by the state of expansion of the bed, and gave the following correlation [6]:

$$d_b = 13.4 u_L^{0.052} u_g^{0.248} \nu^{0.08} \sigma^{0.034} \qquad (2)$$

and

$$v_{br} = 18.0 d_b^{0.0989} \qquad (3)$$

where u_L, u_g, v_{br} are measured in mm/s, d_b in mm, ρ in dyne/cm, and ν in mNs/m^2.

The oxygen transfer rate, N_A, across the liquid film is proportional to the concentration difference existing between the two phases (that is, the driving force, $(C_g^* - C_L)$, and the transfer area, A. The driving force for oxygen transfer within the liquid film is created by the concentration difference between the two sides of the film. The mass transfer rate across the liquid film must equal the transfer rate across the gas film for steady state transfer. That is

$$N_A = k_L A(C_g^* - C_L) \tag{4}$$

The hydrodynamic features of the bioreactor also affects the oxygen transfer rate. The precise spatial (and possibly time dependent) relationship of concentrations and film thickness depends on the hydrodynamics of the bioreactor. Increase in either relative velocity or turbulence level enhance the k_L and reduce the hypothetical distance, δ_L. The theories suggested to explain the oxygen transport across the films include: the penetration theory of Higbie; Danckwertz model, and the boundary layer model, and the two film model of Whitmann. Among these, the two-film theory of Whitmann is the most accepted theory [4, 8]. This theory expresses k_L in different forms using physical parameters. Whitmann assumed the gas and liquid films to be stagnant layers through which oxygen transfer takes place by molecular diffusion and expressed k_L as

$$k_L = \frac{D_L}{\delta_L} \tag{5}$$

The diffusion of oxygen across the liquid film can be modelled mathematically by application of Fick's law, leading to equation (4). This paper focuses on the oxygen transfer from the gas film to the liquid film and within the bulk liquid, where the mass transfer, k_L, is applied.

Detailed knowledge of mass transfer is needed to determine the correct driving force for oxygen transfer. This is because, the determination of the parameters needed for establishing the driving force is prone to erroneous assumptions on the nature of flow of the phases in the three-phase fluidized bed. The other difficulty arises when equilibrium is attained rapidly in the fluidized bed. More emphasis in this study has been on k_La rather than determination of the individual liquid side mass transfer coefficient, k_L, and the interfacial area, a, separately. This is because in the three-phase fluidized bed, it is difficult to distinguish the individual effects of the two

parameters on the overall oxygen transfer rate [9]. Thus it is a common practice (also adopted in this work) to express the oxygen transfer rate using the volumetric oxygen transfer coefficient, k_La, which is the product of the two parameters k_L and a. Thus equation (4) becomes

$$N_A = k_L a(C_g^* - C_L) \tag{6}$$

In this work, the k_La values have been determined using two methods. The first method involved direct measurements of dissolved oxygen concentration in the bioreactor, where the static CSTR and PFR models were used to calculate the k_La values. In the CSTR model, the static measurements of oxygen concentration are modelled as [10]

$$(k_L a)_{CT} = \frac{u_L}{\Delta Z}\left(\frac{C_2 - C_1}{C_g^* - C_2}\right) \tag{7}$$

Equation (7) results from tracer experiments performed by Chatib *et al.*, [9], which indicates that the liquid phase can be considered to be perfectly mixed except within 10 cm of the reactor bottom for a total fluidized bed height in the range of 0.8 - 1.30 m. The equation was derived from an oxygen balance over the mixed zone, giving values of k_La within 10% accuracy. The k_La values calculated from equation (7) are denoted as $(k_La)_{CT}$ in this paper, to distinguish between values from PFR and CSTR models. In their work, a strong dependence of $(k_La)_{CT}$ on gas velocity was revealed.

In the pulg flow model, PFR, the gas phase is regarded to be ideally mixed, liquid motion is described by plug flow model and the k_La is modelled as

$$(k_L a)_{PF} = \frac{u_L}{\Delta Z}\left(\frac{C_g^* - C_1}{C_g^* - C_2}\right) \tag{8}$$

Equation (8) derived from the PFR model, led to the k_La values denoted as $(k_La)_{PF}$ in this paper. The increasing use of oxygen probes in the wastewater treatment works and in various fields has stimulated a growing interest in their fundamental properties and operating principles, details of which are given by Lineck *et al.*, [10].

The second method was by predicting the k_La values from the hydrodynamic

parameters of the three-phase fluidized bed bioreactor. This method led to the values denoted in this work as $(k_La)_h$. The basis of predicting the k_La values from the hydrodynamic parameters lies on the fact that there is a greater analogy between the three fundamental transfer processes, that is mass, heat and momentum transfer. Also, equations incorporating momentum transfer parameters are used in evaluating mass transfer operations because the hydrodynamic parameters are easy to measure accurately.

The importance of the study on effect of air flow rate on oxygen transfer in the three-phase fluidized bed lies on the fact that the particles which shelter the micro-organisms are supported by the momentum transferred from the gas bubbles to the liquid and from liquid to the solids. In this work, the fluidized bed was operating in the concurrent mode, whereby, liquid and gas were simultaneously introduced from the bottom. It is common practice to introduce the gas through a dome-shaped distributor so as to effect uniform flow of the gas across the bed cross-section. This mode of operation corresponds to the most successful industrial application of three-phase fluidized beds like coal liquefaction, hydro-cracking and hydro-sulfurization of heavy crude. Gas flow rate in such reactors is a key factor since it affects the specific values, changes and interdependence of bed porosity, bubble characteristics, mixing, heat and mass transfer [6].

The problems associated with the treatment of wastewater in the three-phase fluidized bed bioreactors like excessive biomass growth and higher energy consumption [11, 12], were taken into account during design of the bioreactor and selection of the biomass support. To maintain high oxygen transfer rate in the bioreactor, experiments were performed to investigate the effect of the operating parameters on the k_La. Presented in this paper is the effect of air flow rate, (expressed as a superficial velocity, u_g, across a column of diameter 0.20 m) on the oxygen transfer in the three-phase fluidized bed bioreactor utilising novel biomass support, that is the KMT^R support, in industrial wastewater treatment.

METHODOLOGY

In this research, wastewater samples were collected from two industries, viz., Tanzania Breweries Ltd., (TBL), and Tanzania-Italy Petroleum Refinery Co., (TIPER), both based in Dar es Salaam. Properties of the

liquids used in this work are given in Table 1.

Table 1 Physical properties of Liquids used

Liquid Source	Tap water	Brewery waste	Refinery waste
Viscosity, *mPa.s*	1.04	1.51	4.25
Density, kg/m^3	994	970	810
pH	6.8	6.3	6.2
COD_o	-	26,000	44,000

Artificial wastewater was made by dissolving selected compounds (like phenol) in distilled water. The major tasks performed are summarized as: pilot plant design, selection of biomass support and establishment of measurement techniques, and experimentation. The study of hydrodynamics of the three-phase fluidized bed bioreactor, and investigation of oxygen transfer rate followed complete design, erection and testing of the pilot plant. The schematic of a pilot plant is shown in Fig. 1, from which FBT is the foam breaker tank, which was mounted at the top to accommodate foam [13], and allow separation of gas due to reduced exhaust pressure. The distributor plate, DP, was a flat plate with 250 holes of 4 mm diameter, having a 10% fractional open area, with a holes density of 8000 holes/m^2 [1]. A non-return valve, NRV, was mounted on the compressed air pipeline to restrict the down flow of liquid into the line.

Liquid from the feed tank, T, was pumped into the column to a required height of slurry (solid and liquid), H_{sL}. While keeping the liquid flow rate constant, compressed air was introduced at the bottom to fluidise the bed. Liquid fluidization was not possible, due to low density of particles, which were floating at the liquid surface for liquids with density above 850 kg/m^3. Throughout treatment time liquid was recycled through the valve, V_4, while keeping the fluidized bed height, H_C, constant. The bioreactor was operated in the range of 3.7 to 42.5 mm/s for air velocity; while the liquid velocity ranged from 0 to 6.6 mm/s. Compressed air pressure, P_g, was varied between 2 to 5 bar, while the liquid height was varied between 1.0 to 3.0 m. Solids loading was varied from 0.5 to 4.5 kg. The total fluidized bed height, H_C, ranged from 1.0 to 6.0 m. All experiments were carried out at room temperature.

Two dissolved oxygen probes (model RL 425, supplied by Russell Laboratory Equipment Co., UK), labeled as DOP in Fig. 2, were used to read directly the dissolved oxygen concentration (mg/l), temperature

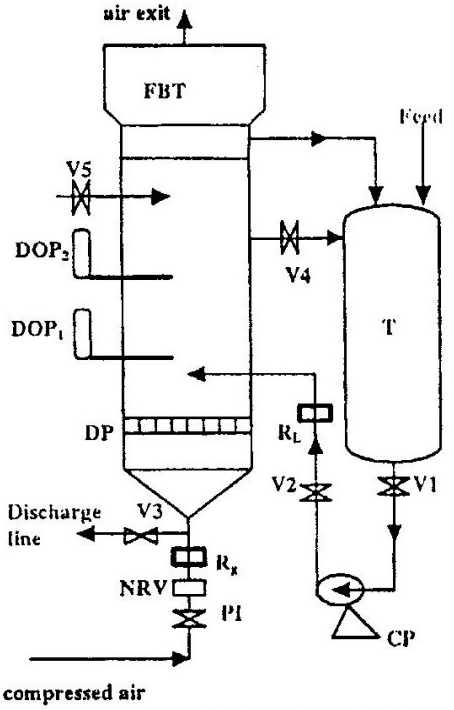

Fig. 1 Schematic of the three-phase fluidised bioreactor pilot plant showing the foam breaker tank and the gas distributor

(°C), and percent saturation in the bulk liquid. The $(k_La)_h$ was determined after aerating the bed for 3 to 5 minutes (to attain equilibrium in the bed) at known values of u_g and u_L. Initial and final bed heights, H_{sL} and H_c, respectively, were recorded for each run, at the end of which the mass of the liquid present in the bed, M_L, was measured after closing the valves V_2 and PI, (fast-close-valve method). Equations utilizing the hydrodynamic parameters of the bioreactor, were used to predict the $(k_La)_h$ values, that is equations (10)-(14). The air hold-up, ε_g, that is, the fraction of the bed volume occupied with air, was calculated from the equation

$$\varepsilon_g = \frac{\Delta H}{H_c} \tag{9}$$

Equation (9) was applied after measuring the change in bed height, ΔH, due to aeration. After measuring M_L, ρ_L, and H_c, liquid phase hold-up, ε_L, was determined from the equation

$$\varepsilon_L = \left(\frac{M_L}{\rho_L}\right)\left(\frac{1}{H_c A_c}\right) \tag{10}$$

The solid phase hold-up, ε_S, was calculated as the difference

$$\varepsilon_s = 1 - \varepsilon_g - \varepsilon_L \quad (11)$$

The $(k_La)_h$ values were calculated from the equation (13) [14],

$$(k_La)_h = 1.154\left(\frac{P_o}{V_R}\right)^{0.79} \quad (12)$$

where

$$\left(\frac{P_o}{V_R}\right) = \frac{g}{\varepsilon_g}[\rho_s\varepsilon_s(u_L + u_g) - \rho_L u_L(1-\varepsilon_L) + \rho_L u_g \varepsilon_L] \quad (13)$$

calculated after determining all the parameters experimentally [15]. Other equations used to predict $(k_La)_h$ values include [5]:

(i) For higher gas flow rates with the ratio $\left(\frac{Q_g}{V_R}\right)$ in the range (6.4 -27) x 10^{-4} s^{-1}, the following equation was used:

$$(k_La)_h = 0.08\left(\frac{Q_g}{V_R}\right)^{0.45} \quad (14)$$

(ii) With $\left(\frac{P_o}{V_R}\right)$ expressed in (kW/m^3), Cooper suggested the equation

$$(k_La)_h = 21.45\left(\frac{Q_g}{V_R}\right)^{0.79} \quad (15)$$

To investigate the effect of k_La on purification efficiency, it was necessary to determine the COD values at different air velocities (at which the corresponding k_La values were known). The purification efficiency, E, was calculated from the equation

$$E = \left(\frac{COD_o - COD_t}{COD_o}\right) \times 100\% \quad (16)$$

Throughout the treatment period, a constant setting of u_g, H_c, u_L and M_s was maintained. The COD values were measured using a digester-photometer unit. The digester was used to heat test tubes containing

wastewater samples from the bioreactor at a temperature of 148°C for 2 hours. The photometer, operated in the wavelength range of 400-800 nm, with two standard filters of 445 and 485 nm, was used to read directly the COD value in ppm after digestion and cooling to room temperature.

RESULTS AND DISCUSSION

Bed expansion

The oxygen transfer rate is high when the porosity of the three-phase fluidized bed is high. An intensive study was done to investigate the variation of the fluidised bed height with air flow rate. An interesting phenomena was the bed expansion upon injection of gas into a liquid-solid slurry. For such light particles used in this work, liquid fluidization was not possible because the particles were floating at the liquid surface. Bed expansion was measured at different air flow rates, results of which are represented in Fig. 2. The bed expansion was expressed as a ratio of aerated bed height to the initial liquid height.

As can be seen in Fig. 2, E_b increased monotonically with air flow rate up to 42.5 mm/s, beyond which the bed height remained practically constant. Further investigation beyond this velocity was not possible because the flow of fluids in the bed were no longer steady and vibrations of the rig-structure was observed. Beyond this velocity, large air bubbles or slugs were formed and the whole bed reached a state of 'churn turbulence', at which the bioreactor exercised intense vibrations. Experimental findings were compared with literature reported by Bergougnou *et al.*, [16]. The difference was observed at air flow rates from 0 to 3 times the minimum fluidization velocity of 8 mm/s.

While Bergougnou *et al.*, [6], expressed bed expansion as a function of the minimum fluidization bed height, H_{mf}, experimental bed expansion was expressed in terms of liquid height before aeration, H_L, since in this work there was no fluidization without air flow.

Initial bed contraction depicted by literature data in Fig. 2 has been explained to be a condition favoured by a high bubble velocity at a given hold-up, and also accelerated by a smaller liquid velocity and a high

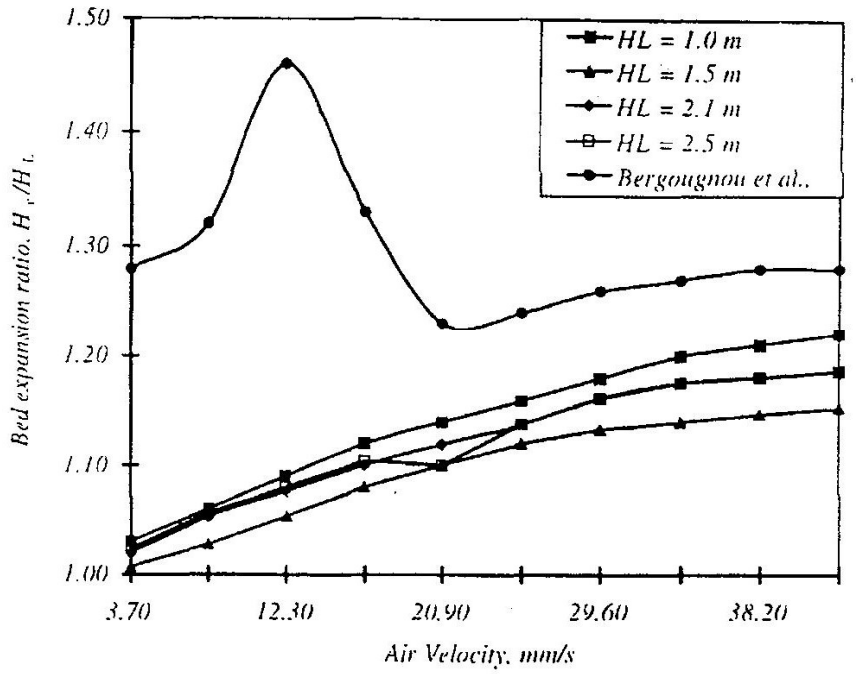

Fig. 2 Plots of experimental bed expansion, $E_b = Hc/H_L$, at different air flow rates, for various values of initial liquid heights in the bioreactor column, H_L, for KMTR support. The results are compared with literature data from aeration of a liquid-fluidized bed of 6 mm cracking catalyst particles with $u_{mf} = 7$ mm/s, $H_{mf} = 1.0$ m, [16].

volumetric ratio (wake volume/bubble volume) [6]. The bed expansion observed in this work can be explained as due to the fact that the KMT^R support was not wetable. Wetability of particles has been reported to affect bed expansion. It has been reported that glass particles of the same physical properties coated with teflon gave bed expansion while non-coated gave bed contraction in the same solution [6]. Other factors leading to the observed bed expansion are low matrix density and large size of the KMT^R support.

Air Hold-ups and Bed Porosity

In this research, effect of air flow rate on the air hold-ups, ε_g, and on bed porosity, $\varepsilon = (\varepsilon_g + \varepsilon_L)$, was examined Fig. 3 and 4. While other workers, proposed semi-empirical methods for estimating bed porosity which agreed with experimental values within 3-6% error, experimental values are reported in this paper without correlation. Since the effect of liquid velocity on oxygen transfer rate is primarily through the air hold-ups [17], a report

on the effect of u_L on air hold-ups is also given. Experimental results revealed that air hold-ups were independent of liquid velocity, Fig. 3. The relationship between u_L and ε_g shows that the choice of u_L could not affect the oxygen transfer rate, and that the air hold-ups were mainly determined by the air flow rate. The rising bubbles were observed to dominate the flow of both phases, acting also as primary agitators and hence responsible for local mixing. The experimental values of air hold-ups and bed porosity observed in this research differ from literature values due to different design of liquid feeding systems and due to accuracy of the technique of measuring. While experimental bed porosity and air hold-ups were based on bed height and liquid-mass measurements, literature values were measured using conductivity probes which can distinguish between bubble gas and continuous liquid phase at the measuring point [18]. Use of glass column eliminated accurate phase hold-up measurements by insertion of pressure taps, suggesting further work using gamma rays absorption and the interfacial area determination by light transmission method.

The bubble size and the interfacial area are mainly determined by the gas flow rate [16]. The variation of air hold-ups is shown to be similar for beds of glass beads, plastic particles and beds of other particle types, whereby, increasing air flow rates increased air hold-ups for all particles at all conditions for both literature as well as experimental values, as shown in Fig. 3 [15, 19]. The lower values of air hold-ups found in
TIPER wastewater depicted in Fig. 3 is attributed to higher viscosity of TIPER wastewater compared to TBL and tap water, as shown in Table 1. These results contradict literature reports that viscosity increased bed porosity for glass beads with $d_p = 6$ mm for u_g ranging from 7 to 56 mm/s at $u_L = 54$ mm/s [20]. For light particles, such as KMT^R support,
the air hold-ups were found to decrease with liquid height, as shown in Fig. 3. The variation of bed porosity with air flow rate is given in Fig. 4. While other workers observed that bed porosity, ε, decreases with u_L, Fig. 4 shows that there was no clear relationship between u_L and ε [15, 19]. The major contribution to the porosity of the bed was the liquid (continuous phase). Since the liquid was allowed to flow down a recycle stream by gravity, the liquid phase hold-up was found to decrease. The contribution of the air hold-up to bed porosity was so small that the bed porosity mainly depended on liquid hold-up, at a constant solids loading. Literature data contradict the findings, probably due to the nature of operation of the bioreactor.

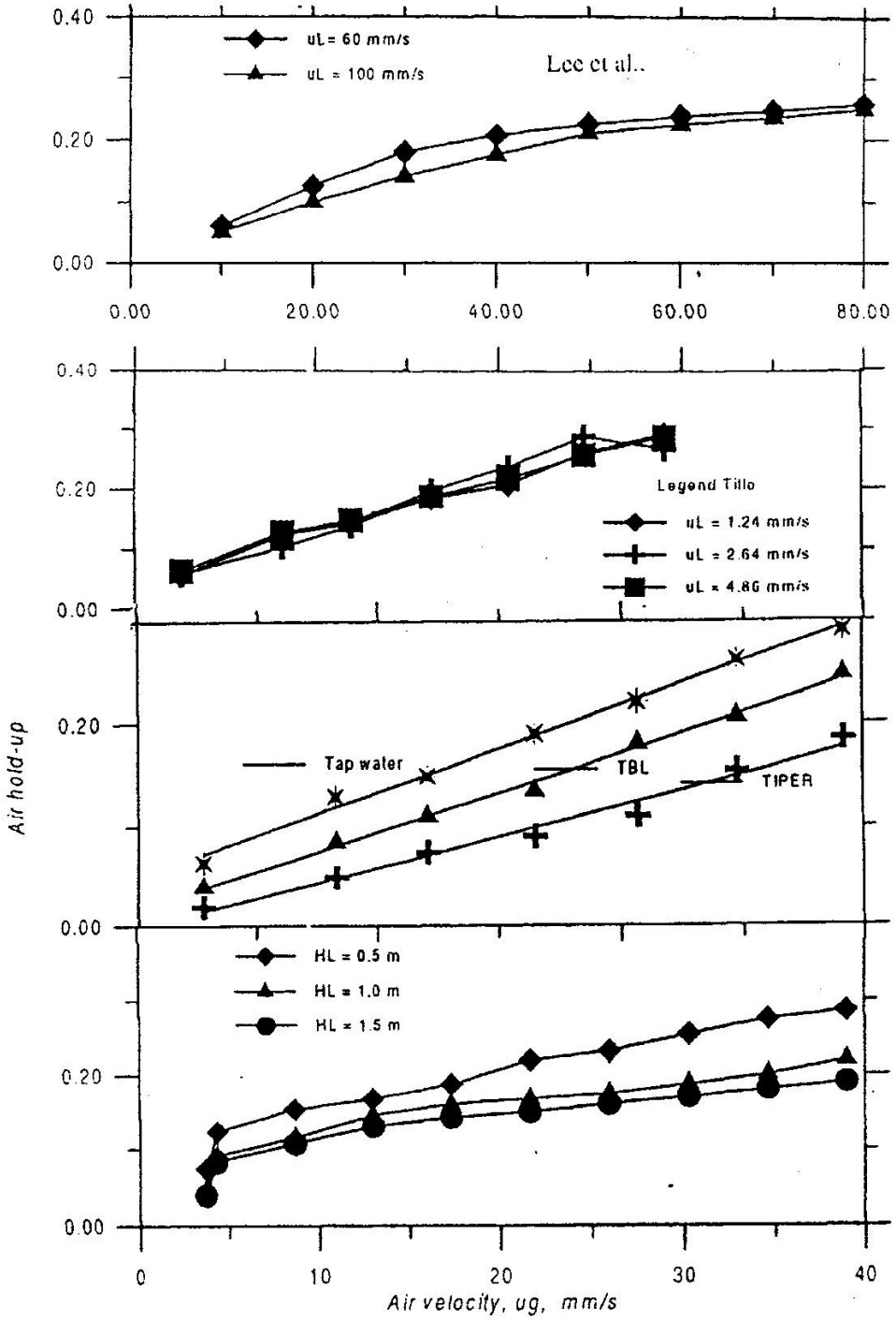

Fig. 3 Variation of experimental gas hold-ups, ε_g, and bed porosity, $\varepsilon = (\varepsilon_g + \varepsilon_l)$ with air flow rate at different liquid velocities, with literature data included for comparison.

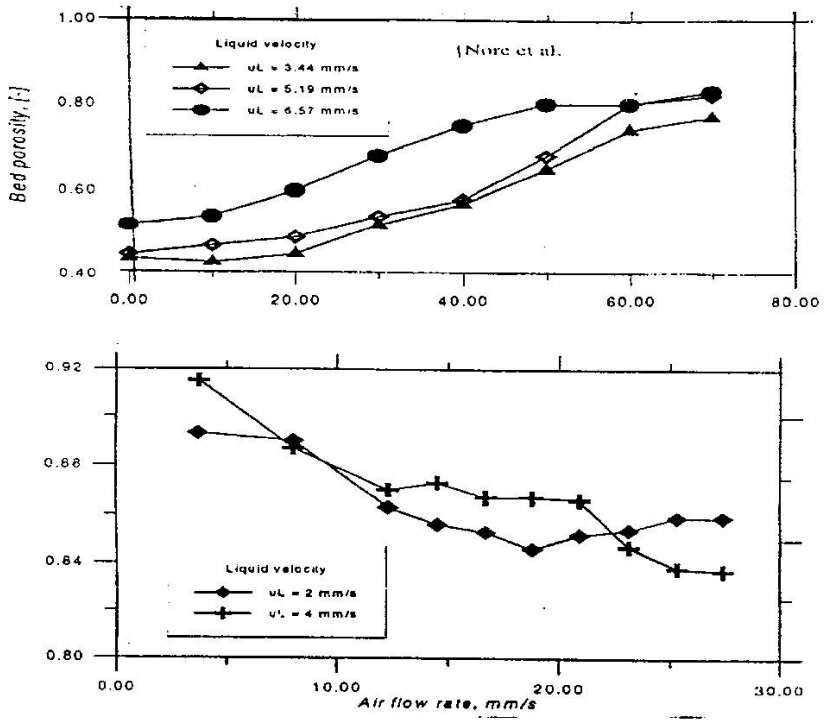

Fig. 4 Plots of bed porosity, $\varepsilon = (\varepsilon_g + \varepsilon_L)$, for the KMTR support when used in a three-phase fluidised bed bioreactor, at a solid mass of 2 kg, at a bed height of 1.88 m, for various liquid velocities

Oxygen Transfer

It was observed that $(k_La)_h$ varied linearly with air velocity at constant liquid flow rate, Fig. 5. Results show that $(k_La)_h$ depends solely on air flow rate. It can be seen from Fig. 5 that increasing the liquid flow rate reduced the $(k_La)_h$. On the other hand, the $(k_La)_{CT}$ values revealed a strong dependence on the air flow rate especially at higher values of u_g, as shown in Fig. 6. It was also observed that air flow rate affected the degree of biomass support distribution in the bed and that air velocity of 8 mm/s was needed to completely suspend 2.0 kg of the KMT^R support in a fluidized state at H_c = 2.0 m. The fluidizing velocity was in turn affected by the mass of solids charged into the bioreactor. The decrease in k_La with liquid velocity was attributed to the fact that, increasing u_L reduces the relative velocity between the fluids and the radial flows of air and water becomes small, lowering the frequency of the bubble subdivision. This suggests that operating the bed with liquid down flow could further enhance $(k_La)_h$ [21].

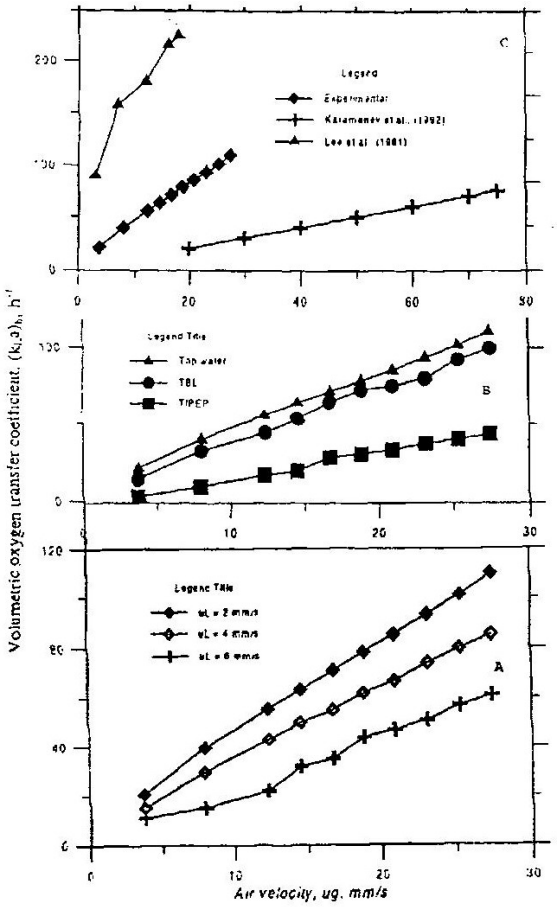

Fig. 5 Variation of (kLa)h with air flow rate (A) different liquid flow rates for tap water, (B) wastewater samples (C) comparison with literature data

By varying the air pressure from 1.5 to 3.8 bar, it was found that $(k_La)_{CT}$ was increasing at all air velocities, Fig. 6. These findings were attributed to the fact that the solubility of oxygen and hence oxygen transfer depends on gas pressure in the gas bubble, as per equation

$$C_g^* = \left(\frac{Y_{o2}}{H}\right) P_g \qquad (18)$$

Thus, increasing P_g increases the saturation oxygen concentration, C_g^*, which in turn increases the driving force, $(C_g^* - C_L)$, as depicted by equations (7), (8) and (17). Results shown in Fig. 6 are in agreement with the report by Chang *et al.*, (1992), [22]. Thus instead of using pure oxygen in improving the rate of oxygen transfer in the wastewater treatment plants, the same purpose can be attained by increasing the air pressure [22].

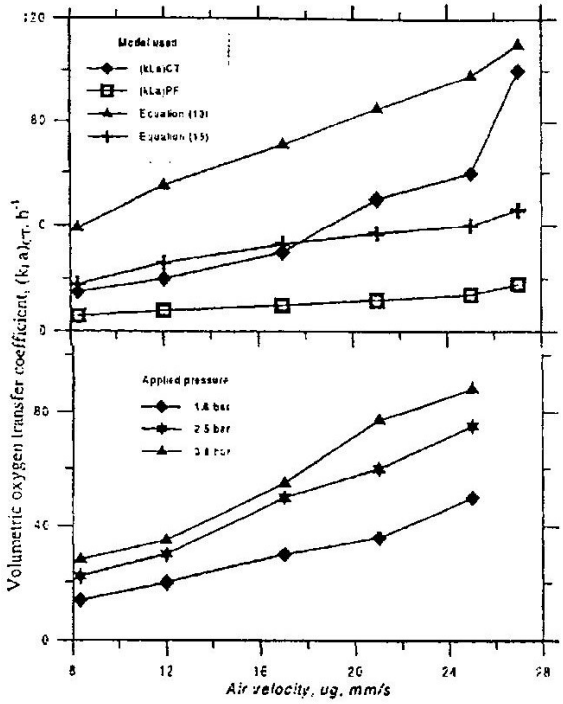

Fig. 6 Values of $(kLa)_{CT}$ at various air flow rates and compressed air pressures, Pg.

Literature observations show that k_La values for carbon monoxide in organic liquids (n-hexane, n-decane, and n-tetradecane) were increasing with gas pressure. Results were attributed to the fact that more volatile liquids decreased partial pressure of carbon monoxide hindering its chance for diffusion. Despite the increase in oxygen transfer as P_g increases, there should be a compromising pressure due to an increased pumping cost.

Comparing $(k_La)_h$, $(k_La)_{PF}$ and $(k_La)_{CT}$, it was found out that $(k_La)_h$ values were higher than both $(k_La)_{PF}$ and $(k_La)_{CT}$, Fig. 6. The CSTR model gave the values which were comparable to $(k_La)_h$ at higher air flow rates. This discrepancy was attributed to the low accuracy in driving force measurements, since the $(k_La)_C$ values rely upon correct measurements of the driving force for mass transfer. Practically, it is difficult to measure correctly the driving force, thus, the mass transfer rate is normally approximated using mass balance techniques [15]. Due to rapidly attained equilibrium in the three-phase fluidized bed in terms of oxygen concentration, the driving force measurements suffer another source of error. The plug flow model failed to explain the nature of flow in the three-phase bioreactor. Visual observation revealed that there was a circular

motion of solids, whereby, solids at the centre of the column were moving upwards while those close to the walls were moving downwards, showing a discrepancy from plug flow.

It was observed that tap water gave highest k_La values at all air flow rates, compared to brewery and refinery wastewater, Fig. 5. This was explained to be caused by high viscosity of the refinery wastewater, as shown in Table 1. Results shown in Fig. 5 agrees with literature findings that k_La is inversely proportional to the liquid viscosity [4]. These results were accompanied by the findings that brewery wastewater was easy to treat, giving a purification efficiency of 86% compared to the refinery wastewater which where only 40%, purification efficiency was obtained.

High literature k_La values are reported in artificial wastewater, made by introducing a specific component in distilled water. While Lee *et al.*, [15], used octanol solution in water as a liquid, industrial wastewater comprising of several components was used in this work. The k_La values reported by Karamanev *et al.*, [23], were comparable to those found in this research, because industrial wastewater was used in both cases. Comparing experimental values calculated from different equations, it was found out that equation (14) gave average k_La values between those from equations (7), (8) and (12).

CONCLUSION

From the above findings, it can be concluded that:

1) The air flow rate is the major factor which determines the k_La values at all operating conditions of the three-phase fluidised bed bioreactor utilising KMT^R support .

2) The k_La values decreases with increasing liquid flow rate. Thus, treatment of industrial wastewater must be done at lowest possible liquid flow rate to achieve high degradation efficiency of pollutants in wastewater.

3) The discrepancy between k_La values from dissolved oxygen concentration measurements and hydrodynamic parameters measurements has been attributed to difficulties in measuring the driving force for mass transfer.

4) Other methods for determination of k_La values like the sodium sulphite and the hydrazine methods are also recommended here to get more reliable results prior to design of industrial bioreactors.

5) Results reveal that treatment of wastewater in the three-phase fluidised bed with KMT^R support, should be done at higher air flow rates to achieve higher rate of oxygen transfer.

6) The use of KMT^R support is highly recommended due to the fact that it offers bed expansion and high air hold-ups.

7) Higher air pressure increases k_La, suggesting an option of using compressed air at higher pressure instead of pure oxygen.

NOTATIONS

A - transfer surface area, m^2
Ac - cross-sectional area of the column
a - interfacial surface area, m^2
C_1, C_2 - oxygen concentrations at bottom and top of the fluidised bed, mg/l
C_g* - saturation oxygen concentration in the liquid at the interface, mg/l
C_L - oxygen concentration in the bulk liquid, mg/l
COD_o - initial COD, mg/l
D_c - column diameter, m
D_L - diffusivity of oxygen in water, m^2/s
d_p - equivalent particle size, mm
E - COD removal efficiency, %
g - acceleration due to gravity, m/s^2
H - Henry's Law constant, atm.litre/mg
H_c - fluidized bed height, m
H_L - liquid height in the column, m
H_{sL} - bed height before aeration, m.
H - change in bed height due to aeration, m.
k_L - mass transfer coefficient for liquid phase, m/s.
k_La - volumetric oxygen mass transfer coefficient, h^{-1}
$(k_La)_h$ - k_La determined from the hydrodynamics of the three-phase bioreactor

$(k_La)_{CT}$ - k_La determined from oxygen concentration measurements, using CSTR model
$(k_La)_{PF}$ - k_La determined from oxygen concentration measurements, using PFR model
M_L - mass of liquid in the bioreactor column
(P_o/V_R) - power consumed in aerating the bioreactor, W/m^3.
Q_g - air flow rate, m^3/s
u_L - liquid velocity, m/s
u_g - air velocity, m/s
V_R - bioreactor volume, m^3
Y_{O2} - mol fraction of oxygen in the liquid phase

Greek letters

Z - istance between oxygen concentration probes along the fluidised bed, m.
δ_L - liquid film thickness, m.
ε_g - air hold-up, %
ε_L - liquid phase hold-up,
ε_s - solid phase hold-up
ρ_s - density of support particles, kg/m^3

Abbreviations

COD - Chemical oxygen Demand
CSTR - continuously Stirred Tank Reactor
DOC - Dissolved Oxygen Concentration, ppm
KMT - Kaldnes MiljØ Teknologi Co., Norway.
TBL - Tanzania Breweries Ltd.
TIPER - Tanzania-Italian Petroleum Refinery Co.

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