1 **Modification of oxygen transfer rates in activated sludge with its characteristic**
2 **changes by the addition of organic polyelectrolyte**

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13

14 **Abstract**

15 The present study focused on the influence of the apparent viscosity of
16 activated sludge on mixed liquor oxygen transfer rates, and examined whether both
17 could be modified by the addition of an organic polyelectrolyte. Batch experiments
18 carried out using mixed liquor samples in stirred tank reactors revealed that α -factors,

which incorporate any difference in oxygen mass transfer coefficient values between clean water and mixed liquor samples, showed exponential relationships when plotted against increases in mixed liquor apparent viscosities and sludge mixed liquid suspended solids values. Furthermore, oxygen mass transfer coefficients increased exponentially with increases in the Reynolds number, a parameter which reflects liquid turbulence levels. Oxygen mass transfer rates of five sludge samples collected from four full scale wastewater treatment plants (WWTPs) also increased by about 10% after flocculation, while with a sludge sample collected from the lab scale reactor, it decreased by about 5%. One likely explanation is that the apparent viscosities of the WWTPs and the lab-reactor sludges decreased and increased respectively after flocculation. Such changes probably reflect changes in the volume fraction of mixed liquor suspended solids as indicated by changes in sludge volume indices, particle size values and endogenous respiration rates before and after flocculation. These findings assist in developing an understanding of how oxygen mass transfer characteristics may be affected by activated sludge suspensions, and hence assist in reducing the operational costs of WWTPs.

Keywords

37 Activated sludge; α -factor; Flocculation; Floc volume; Oxygen transfer; Viscosity

38

39 **1. Introduction**

40 Membrane bioreactors (MBR) have been used increasingly in wastewater
41 treatment to minimize the solid phase –liquid phase separation problems often
42 encountered in conventional activated sludge (CAS) clarifiers [1]. MBR systems also
43 have the advantage of operating at high mixed liquid suspended solids (MLSS)
44 concentrations, generating a reduced excess sludge production, and allowing reuse of
45 the treated water [2]. However, biological aeration requirements in MBR are higher than
46 in CAS because of the lower oxygen mass transfer rates achievable with their higher
47 MLSS concentration. The main power requirement comes from the aeration system
48 used to maintain high dissolved oxygen (DO) levels and keep the solids in suspension
49 [3-6].

50 Several studies have investigated the correlation between oxygen transfer rates
51 and MLSS levels in activated sludge systems, where an increase in MLSS has resulted
52 in a corresponding linear or exponential decreases in the oxygen mass transfer
53 coefficient (k_La) and α -factor [4-5,7-10]. The α -factor is necessary as a correction factor,
54 which incorporates any difference in k_La values between clean water and mixed liquor

samples. However, large variations in the k_La and α -factor values at a single MLSS concentration have been reported, suggesting MLSS concentration is not the most suitable parameter for correlating k_La and α -factors. Besides, any increase in apparent viscosity (μ_{ap}) seems to result in an exponential decrease in the α -factor, irrespective of the origins of the sludge used in these studies [9,11].

Addition of organic polyelectrolytes to act as filter aids or membrane antifouling agents in MBRs has been reported [12-20]. Furthermore, some organic polyelectrolytes have been reported to increase oxygen transfer rates in activated sludge [15,20]. Adding flocculants to activated sludge system is considered to modify mixed liquor properties by inducing complex changes among the soluble, colloidal and solid fractions [15]. If their addition can decrease both the μ_{ap} and oxygen transfer rates as suggested by others [15,20], it may then be possible to increase the latter, not by decreasing MLSS concentrations, but by decreasing μ_{ap} .

Thus the aim of this study was to understand better the possible correlation between oxygen transfer rates, MLSS levels and μ_{ap} of activated sludge and to see if it is possible to improve oxygen transfer rates by modifying activated sludge characteristics by the addition of organic polyelectrolytes. Firstly, oxygen transfer rates in samples collected from several wastewater treatment plants (WWTP) were measured in a stirred

tank reactor and the relationship between these and the corresponding values of MLSS and μ_{ap} were determined. In addition any possible impact of the sludge rheological properties on oxygen transfer rates was investigated by calculating the dimensionless Reynolds number, an indication of turbulence, for each. Any effects of organic polyelectrolyte addition on oxygen mass transfer rates and activated sludge μ_{ap} , particle size, sludge volume index (SVI), pH and endogenous respiration rates were also examined.

2. Materials and methods

2.1 Activated sludge samples and experimental set-up

Five activated sludge samples were collected from three municipal WWTPs and a lab scale reactor. Table 1 shows the operational details of these WWTPs and the lab scale (30 L) reactor. All activated sludge samples were transferred to a stirred tank reactor right after the samples were obtained and the configuration of the reactor is shown in Fig. 1. The glass column reactor (155 mm of internal diameter (ID) and 270 mm in height) had an effective working volume of 4 L (155 mm ID and 212 mm in height). It was equipped with a six-blade Rushton turbine impeller (bottom side), a four-blade paddle impeller with 45° pitch (upper side), and four baffles. The diameter of

the turbine impeller was 65 mm. and its width was 15 mm, while the paddle impeller diameter was 80 mm. and 15 mm wide. The distance between each impeller was 160 mm and the turbine impeller was located 20 mm from the vessel base. The baffles were 270 mm high and 10 mm wide. A sparger (ceramic air stone NR-D60, IWAKI, Tokyo, Japan) 50 mm in diam. was 14 mm thick with a mean pore size of 80 μm , and was located centrally at the vessel base.

All experiments were performed in a water bath at $20\pm0.1^\circ\text{C}$ maintained with recirculating chiller (CTP-1000, TOKYO RIKAKIKAI, Tokyo, Japan). The pH and temperature meter (HM-21P with GST-2729C probe, TOA-DKK, Tokyo, Japan) and the dissolved oxygen (DO) meter (DO-24P with OE-270AA galvanic probe, DKK- TOA, Tokyo, Japan) were operated on line, as indicated in Fig. 1. The input air flow rate was set manually at 1 L min^{-1} by a mass flow meter (Kofloc, Kyoto, Japan) during measurement. A pressure regulator was used to maintain the inlet air pressure at 0.1 MPa for most air flow rates.

2.2 Oxygen transfer coefficient and α -factor determinations

The k_La in activated sludge was determined by the dynamic method [21]. Each activated sludge sample was centrifuged (3000 rpm (1650 g), 2 min) and concentrated

up to a 20 g L⁻¹ MLSS level before being diluted to the required concentration using the supernatant of centrifuged mixed liquor as diluent. MLSS, particle size distribution, mean particle size, SVI, μ_{ap} and density were determined for all these sludge samples, while μ_{ap} was determined for each supernatant, as described in section 2.5. When sludge samples were transferred to the stirred tank reactor, agitation (240 rpm) and aeration (1 L min⁻¹) were then started. As soon as the DO concentration reached equilibrium, aeration was stopped, and endogenous oxygen uptake rates (OUR_{en}) (mgO₂ g-MLSS⁻¹ h⁻¹) were measured. Each OUR_{en} was calculated from the linear rate of decrease of the dissolved oxygen concentration above the value at which the rate of oxygen utilization became dependent on DO (critical DO concentration) [22]. Before the DO had fallen below its critical concentration, aeration was restarted, the increasing DO concentration was measured over time and the $k_L a$ calculated. The mass transfer balance is given by the following equation:

$$\frac{dC_L}{dt} = k_L a (C_L^* - C_L) - OUR_{en} x \quad (1)$$

Where C_L is measured DO concentration, C_L^* is the saturation DO concentration, and x is MLSS concentration. Eq. 1 can be rearranged to Eq. 2.

$$C_L = -\frac{1}{k_L a} \left(\frac{dC_L}{dt} + OUR_{en} x \right) + C_L^* \quad (2)$$

The $k_L a$ was determined from the slope of the straight line obtained from a plot of C_L

against $dC_L/dt + OUR_{en} x$. The α -factor was calculated by dividing the mixed liquor $k_L a$ by the $k_L a$ of tap water used as control as in the following equation.

$$\alpha = \frac{k_L a_{\text{mixed liquor}}}{k_L a_{\text{tap water}}} \quad (3)$$

2.3 Agitation Reynolds number (Re) measurement

The agitation Re which measures the rheological properties of the mixed liquor was calculated according to Eq. 4.

$$Re = \frac{D_I^2 N \rho}{\mu_{ap}} \quad (4)$$

Where, D_I , N , ρ , and μ_{ap} are the diameter of impeller (m), rotation rate of impeller (s^{-1}), fluid density ($kg\ m^{-3}$), and apparent viscosity (Pa s).

2.4 Effect of adding flocculant on oxygen transfer coefficient determinations

The $k_L a$ values before and after flocculation of each activated sludge sample (Table 1) were determined as described in section 2.2. All mixed liquor samples were diluted to $10\ g\ L^{-1}$ MLSS level when the $k_L a$ was determined before adding flocculant. Agitation in the reactor was stopped and then 500 ml of supernatant was removed. The baffles in the reactor were removed and agitation (180 rpm) was then restarted upon addition of 500 ml (1% of MLSS) of the cationic dimethylaminoethyl acrylate

polyelectrolyte solution (ICM4204NG2, Ishigaki maintenance, Tokyo, Japan). After a rapid agitation period (180 rpm, 5 min), a slower agitation rate was imposed (50 rpm, 15 min). The k_{La} in flocculated activated sludge was then measured as before. The polyelectrolyte was dissolved in milliQ water with agitation for 24 h and the stock solution was prepared to 500 mg L⁻¹.

2.5 Analytical methods

The MLSS and SVI were measured according to standard methods [23]. Particle size distributions and mean particle sizes were measured with a laser diffraction/scattering particle size distribution analyzer LMS-24 (Seishin enterprise, Tokyo, Japan). The μ_{ap} of concentrated sludge suspensions and their supernatants were measured in triplicate using a rotary viscometer (TVC-7 with rotors no. 0 and no. 1, Toki sangyo, Tokyo, Japan) at a fixed rotating speed (20 rpm) and Ostwald viscometer, respectively. Activated sludge samples were incubated with agitation in a water bath at $20 \pm 0.1^\circ\text{C}$, and the μ_{ap} of sludge suspension was measured at the shear rate of 7.1 s⁻¹ (rotor no. 1) or 17.5 s⁻¹ (rotor no. 0) for 30 s when agitation was stopped. The shear rates were calculated according to Eq. 5.

$$\gamma = \frac{0.209N_r}{1 - \left(\frac{R_b}{R_c}\right)^2} \quad (5)$$

Where, γ , N_r , R_b , and R_c are the shear rate (s^{-1}), rotation rate of rotor (rpm), radius of rotor (m), and radius of cylinder (m). Viscosity of a 15 ml aliquot of the supernatant obtained after centrifugation (3000 rpm (1650 g), 3 min) was examined with an Ostwald viscometer in a water bath at $20 \pm 0.1^\circ\text{C}$.

3. Results and Discussion

3.1 Relationship between oxygen transfer rates and activated sludge sample characteristics

3.1.1 MLSS vs α -factor

The k_La of tap control sample was estimated in duplicate. The mean value (0.594) was then used for the calculation of the α -factor. The α -factor was compared with the MLSS concentrations ranging from 5-20 g L^{-1} . An increase in MLSS over a 5-20 mg-L^{-1} range resulted in either a linear or exponential decrease in the α -factor for all the examined activated sludge samples, as shown in Fig. 2. Such relationships between MLSS concentration and the α -factor (i.e. linear or exponential decreases) have been noted in other studies [4-5, 9-11]. However, these were undertaken in tanks of

different geometries using a range of different aeration devices, which would generate different energy dissipation rates and shear stresses [4]. The fall in oxygen transfer rates as MLSS concentration increased differed with each sludge sample. Here the α -factor of three sludge samples (WWTP A (Conv), WWTP A (A₂O), and WWTP B) showed almost identical trends. However, those for the lab scale reactor and WWTP C sludges were markedly different. Although both had a very similar α -factor value (approx 0.8) at 5 g L⁻¹ of MLSS concentration, the WWTP C sample value decreased sharply as MLSS concentrations increased and decreased to close to zero at 20 g L⁻¹ of MLSS concentration. This trend was also seen with the other WWTP sludge samples, although the lab reactor sludge showed a moderate α -factor decrease as MLSS concentrations increased, and its α -factor was close to 0.6 at 20 g L⁻¹ of MLSS concentration. These outcomes suggest that the oxygen transfer rate coefficient was affected not only by the aeration device but also by the characteristics of the activated sludge, since all the experiments discussed here were conducted using the same aeration device.

When two of the activated sludge samples from WWTP B were again analyzed after three months (Fig. 2) , their α -factors were very close at similar MLSS values (around 5 and 10 g L⁻¹), suggesting a high reproducibility of the oxygen transfer measurements in this study.

3.1.2 Correlation between activated sludge viscosity and α -factor

When α -factor values were compared to the corresponding μ_{ap} the following outcomes were seen. Fig. 3 shows the relationships between μ_{ap} at a shear rate of 7.1 s^{-1} and α -factor values for the samples shown in Fig. 2, for which the MLSS was adjusted as shown in Table 2. Some samples shown in Fig. 2 are not represented in Fig. 3 because their apparent viscosities were not measured. In Fig. 3, an increase in μ_{ap} for all examined activated sludge samples resulted in an exponential decrease in their α -factor values, which suggests that its value is determined by the μ_{ap} irrespective of the origin of the sample analysed. Gnder [11], Krampe and Krauth [9], and Rosenberger et al. [24] have all reported a correlation between α -factor and μ_{ap} . Furthermore, the relationships between them followed a similar exponential curve (i.e. $\alpha = \mu_{ap}^{-0.45}$ by Gnder [11]; $\alpha = \mu_{ap}^{-0.456}$ by Krampe and Krauth [9]) to that found here ($\alpha = 2.11 \mu_{ap}^{-0.384}$). This was despite them applying different reactor shear rates (i.e. Krampe and Krauth [9], 40 s^{-1} and Rosenberger et al. [24], 80 s^{-1}) to those used in our study (7.1 s^{-1}). In this present study, most α -factor values did not fit onto an exponential curve when plotted against MLSS values (Fig. 2) although most fitted an exponential curve when plotted against the determined μ_{ap} values (Fig. 3).

3.1.3 Influence of rheological properties on oxygen transfer rates

To investigate the influence of sludge rheological properties on oxygen transfer rates, the relationship between agitation Re and k_La was explored by increasing the rotation rate of the impeller (N) in the stirred tank from 50 min^{-1} to 240 min^{-1} . Fig. 4 shows the relationship between the N and k_La . As expected, an increase in impeller rotation rate resulted in an increase in k_La for all the examined activated sludge samples and the control sample. Fig. 5 shows the relationship between k_La and Re calculated from Eq. 4. It is clear that increasing Re results in an increase in k_La , and the relationship between them (shown with a black line) was determined from the following:

$$k_La = 0.0207Re^{0.416} \quad (6)$$

The relationship between the calculated (Eq. 6) and measured k_La values is shown in Fig. 6, suggesting that measured k_La values have an error of about 20%. Thus, Eq. 6 seems appropriate for predicting oxygen mass transfer coefficients in the stirred tank reactor.

3.2 Influence of adding organic polyelectrolytes on activated sludge characteristics and

233 *oxygen transfer rates*

234 Based on previously reported data, it is hypothesized that oxygen mass
235 transfer rates in activated sludge will increase if flocculant addition decreases the μ_{ap} .
236 Accordingly, k_La value of the activated sludge was compared before and after addition
237 of the cationic flocculant dimethylaminoethyl acrylate polyelectrolytes (Table 3). The
238 data show that the k_La values of the sludge samples obtained from WWTP A (Conv.),
239 WWTP A (A₂O), WWTP B, WWTP C, and WWTP D increased after polymer addition,
240 by 116%, 111%, 109%, 110%, and 113%, respectively. In contrast the k_La of lab scale
241 reactor sludge decreased, slightly to 95% of its original value. At a shear rate of 17.5 s⁻¹,
242 the μ_{ap} values of sludge samples obtained from WWTP C and WWTP D decreased after
243 flocculant addition, but not that of the lab reactor sludge. Thus, it seems that whether
244 flocculant addition improves the k_La in activated sludge depends on whether it reduces
245 correspondingly the μ_{ap} value.

246 Table 3 also shows the μ_{ap} values for the supernatant phase before and after
247 flocculant addition, where the differences between the respective values are much lower.
248 Therefore, the changes in μ_{ap} values seem to depend largely on changes to the physical
249 properties of the suspended solids phase, and not the liquid supernatant. In some
250 previous studies [15,25], a decrease of 13% in the oxygen transfer rate was reported for

activated sludge samples to which polyaluminium chloride (PAC) had been added.

Furthermore, the mixed liquor viscosity increased slightly, while the supernatant viscosity did not change [26]. Therefore, these data [15] also seem to suggest that changes to sludge particle size and shape might lead to a decrease in oxygen mass transfer rates following flocculant addition.

Many models have been used to determine suspension viscosity. Most of these essentially extend the work of Einstein on spheres, and use his equation [27]:

$$\mu_{ap} = (1 + 2.5\varphi)\mu_0 \quad (7)$$

where φ is the volume fraction of the solid phase in a solid–liquid mixture, and μ_0 is liquid viscosity with no suspended solids. Equation 7 means that μ_{ap} is a linear function of φ , although it was derived based on several theoretical assumptions. These included no effect on viscosity of particle size nor of particle position [28]. As shown in Table 3, the mean particle sizes of all activated sludge samples increased after flocculant addition, again as expected, while only the SVI of the lab reactor sludge increased. This suggests that all WWTP sludge flocs became denser after polyelectrolyte addition, while the lab reactor sludge flocs were more diffuse. As floc densities of the WWTP sludges increased, these volume fractions decreased, as did their μ_{ap} according to Eq. 7. On the other hand, as the floc density of lab reactor sludge decreased, the volume

fraction and μ_{ap} increased. The differences in flocculation between WWTP sludges and lab reactor sludge may depend on the pH of activated sludge. Gill and Herrington (1989) [29] have investigated the effect of pH on kaolin suspensions flocculated with cationic polyacrylamides, which were prepared by copolymerisation of acrylamide and dimethylaminoethyl acrylate quaternised with methyl chloride. They reported that large flocs and clear supernatants after flocculation were achievable at pH values below 7. In this present study, the pH values of WWTP sludges were around 7, while that of the lab reactor sludge was above 8 (Table 3), and only the lab reactor sludge seemed to show poor flocculation characteristics.

Moreover, Table 3 shows a slight decrease in the endogenous respiration rate of all the WWTPs sludge but not the lab reactor sludge, after flocculant addition. This result supports the view that flocs in the WWTP sludges were denser than they were in the lab reactor sludge, since respiration rates would depend on the extent of their contact area with oxygen. Also, some WWTP sludges showed a shift in their pH values from neutrality to mild acidity after flocculation (Table 3), while with the lab reactor sludge the pH was close to neutrality. Iversen *et al.* (2009) [15] reported that the decrease in endogenous oxygen mass transfer uptake rates after flocculation could be explained by a pH shift. Therefore, with high density flocs and a pH shift, bacterial respiration rate

would be affected by more than the apparent viscosity of activated sludge. Although exogenous oxygen uptake rates were not investigated in this study, as any decrease in bacterial respiration rate (i.e. endogenous and exogenous oxygen uptake rates) would lead to a lower treatment efficiency, further investigation on the influence of flocculation not only on oxygen mass transfer rates but also on bacterial respiration rates should be performed.

As mentioned in Eq. 7, an increase in φ of the solid phase in a solid–liquid mixture increases μ_{ap} , which reduces Re , as shown in Eq. 4. A low Re would maintain the flow in a reactor in a laminar state, thus ensuring the air bubbles remain large. Therefore, it can be hypothesized that any reduction of the interfacial area between the air bubbles and liquid phase would lead to a lower k_La value. Henkel *et al.* [30] have reported that an increase in φ itself may lead to the decrease of k_La . They quoted a review [31] and summarized several influence of φ on oxygen transfer rates as resulting from two phenomena; a reduction of turbulence in the bubble wake area, and suppression of the oxygen transfer from the bubble to the liquid phase. Further investigations should determine which of these phenomena is most responsible for the k_La changes recorded here.

Conclusions

- The α -factors are mainly influenced by not the MLSS concentration but the μ_{ap} values.
- There is an exponential correlation between the k_La of activated sludge and the Reynolds number of the stirred tank reactor. The correlation should not depend on the reactor scale because the Reynolds number is a dimensionless parameter which reflects liquid turbulence levels.
- Whether flocculant addition improved the k_La in activated sludge depended upon whether it reduced correspondingly the μ_{ap} value. Such a change in μ_{ap} depended largely not on the supernatant viscosity but on the volume fraction of suspended solids, measured as SVI, particle size and endogenous respiration rates.
- Any encouragement of high density floc formation may reduce the overall bacterial respiration rate in the mixed liquor.

Acknowledgment

The authors gratefully acknowledged Prof. Robert Seviour for his proofreading of the manuscript. The authors also express their gratitude to Mr. Shizuo Furukawa who helped to set up the stirred tank system. The Environmental Planning Bureau of

Yokohama City Government are acknowledged for their provision of activated sludge.

Dr. Kenzo Sugaya and Mr. Masayoshi Katayama are also acknowledged for their provision of polyelectrolytes ICM4204NG2.

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Figure captions

Fig. 1 Schematic diagram of the stirred tank system used in this study.

Fig. 2 Plots of decrease in α -factor values with increase of MLSS. The figure shows the data obtained in this present study and those from previous studies. Two of the activated sludge samples from WWTP B indicated by arrows were again analyzed after three months to check the reproducibility of the oxygen mass transfer measurements.

Fig. 3 Decreases in α -factor values with mixed liquor apparent viscosity (μ_{ap}). Each μ_{ap} represents the mean value of three measurements. The agitation rate of the stirred tank system was maintained at 240 rpm and the shear rate for the measurement of μ_{ap} was set at 7.1 s^{-1} .

Fig. 4 Increase in k_La values with increasing impeller rotation rate (N). Each legend shows sample origin, apparent viscosity, and MLSS in series. The apparent viscosities of lab scale reactor sludge ranged between 12.1-46.7 mPa s achieved by changing the MLSS (10-20 g L⁻¹).

Fig. 5 Correlation between k_La and agitation Reynolds number (Re).

Fig. 6 Correlation between measured k_La (k_La (Exp)) and calculated k_La (k_La (Cal)). The solid line illustrates the close agreement of k_La (Exp) and k_La (Cal) and the dashed lines show the error $\pm 20\%$.

1 **Modification of oxygen transfer rates in activated sludge with its characteristic**
2 **changes by the addition of organic polyelectrolyte**

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13

14 **Abstract**

15 The present study focused on the influence of the apparent viscosity of
16 activated sludge on mixed liquor oxygen transfer rates, and examined whether both
17 could be modified by the addition of an organic polyelectrolyte. Batch experiments
18 carried out using mixed liquor samples in stirred tank reactors revealed that α -factors,

which incorporate any difference in oxygen mass transfer coefficient values between clean water and mixed liquor samples, showed exponential relationships when plotted against increases in mixed liquor apparent viscosities and sludge mixed liquid suspended solids values. Furthermore, oxygen mass transfer coefficients increased exponentially with increases in the Reynolds number, a parameter which reflects liquid turbulence levels. Oxygen mass transfer rates of five sludge samples collected from four full scale wastewater treatment plants (WWTPs) also increased by about 10% after flocculation, while with a sludge sample collected from the lab scale reactor, it decreased by about 5%. One likely explanation is that the apparent viscosities of the WWTPs and the lab-reactor sludges decreased and increased respectively after flocculation. Such changes probably reflect changes in the volume fraction of mixed liquor suspended solids as indicated by changes in sludge volume indices, particle size values and endogenous respiration rates before and after flocculation. These findings assist in developing an understanding of how oxygen mass transfer characteristics may be affected by activated sludge suspensions, and hence assist in reducing the operational costs of WWTPs.

Keywords

37 Activated sludge; α -factor; Flocculation; Floc volume; Oxygen transfer; Viscosity

38

39 **1. Introduction**

40 Membrane bioreactors (MBR) have been used increasingly in wastewater
41 treatment to minimize the solid phase –liquid phase separation problems often
42 encountered in conventional activated sludge (CAS) clarifiers [1]. MBR systems also
43 have the advantage of operating at high mixed liquid suspended solids (MLSS)
44 concentrations, generating a reduced excess sludge production, and allowing reuse of
45 the treated water [2]. However, biological aeration requirements in MBR are higher than
46 in CAS because of the lower oxygen mass transfer rates achievable with their higher
47 MLSS concentration. The main power requirement comes from the aeration system
48 used to maintain high dissolved oxygen (DO) levels and keep the solids in suspension
49 [3-6].

50 Several studies have investigated the correlation between oxygen transfer rates
51 and MLSS levels in activated sludge systems, where an increase in MLSS has resulted
52 in a corresponding linear or exponential decreases in the oxygen mass transfer
53 coefficient (k_La) and α -factor [4-5,7-10]. The α -factor is necessary as a correction factor,
54 which incorporates any difference in k_La values between clean water and mixed liquor

samples. However, large variations in the k_La and α -factor values at a single MLSS concentration have been reported, suggesting MLSS concentration is not the most suitable parameter for correlating k_La and α -factors. Besides, any increase in apparent viscosity (μ_{ap}) seems to result in an exponential decrease in the α -factor, irrespective of the origins of the sludge used in these studies [9,11].

Addition of organic polyelectrolytes to act as filter aids or membrane antifouling agents in MBRs has been reported [12-20]. Furthermore, some organic polyelectrolytes have been reported to increase oxygen transfer rates in activated sludge [15,20]. Adding flocculants to activated sludge system is considered to modify mixed liquor properties by inducing complex changes among the soluble, colloidal and solid fractions [15]. If their addition can decrease both the μ_{ap} and oxygen transfer rates as suggested by others [15,20], it may then be possible to increase the latter, not by decreasing MLSS concentrations, but by decreasing μ_{ap} .

Thus the aim of this study was to understand better the possible correlation between oxygen transfer rates, MLSS levels and μ_{ap} of activated sludge and to see if it is possible to improve oxygen transfer rates by modifying activated sludge characteristics by the addition of organic polyelectrolytes. Firstly, oxygen transfer rates in samples collected from several wastewater treatment plants (WWTP) were measured in a stirred

tank reactor and the relationship between these and the corresponding values of MLSS and μ_{ap} were determined. In addition any possible impact of the sludge rheological properties on oxygen transfer rates was investigated by calculating the dimensionless Reynolds number, an indication of turbulence, for each. Any effects of organic polyelectrolyte addition on oxygen mass transfer rates and activated sludge μ_{ap} , particle size, sludge volume index (SVI), pH and endogenous respiration rates were also examined.

2. Materials and methods

2.1 Activated sludge samples and experimental set-up

Five activated sludge samples were collected from three municipal WWTPs and a lab scale reactor. Table 1 shows the operational details of these WWTPs and the lab scale (30 L) reactor. All activated sludge samples were transferred to a stirred tank reactor right after the samples were obtained and the configuration of the reactor is shown in Fig. 1. The glass column reactor (155 mm of internal diameter (ID) and 270 mm in height) had an effective working volume of 4 L (155 mm ID and 212 mm in height). It was equipped with a six-blade Rushton turbine impeller (bottom side), a four-blade paddle impeller with 45° pitch (upper side), and four baffles. The diameter of

the turbine impeller was 65 mm. and its width was 15 mm, while the paddle impeller diameter was 80 mm. and 15 mm wide. The distance between each impeller was 160 mm and the turbine impeller was located 20 mm from the vessel base. The baffles were 270 mm high and 10 mm wide. A sparger (ceramic air stone NR-D60, IWAKI, Tokyo, Japan) 50 mm in diam. was 14 mm thick with a mean pore size of 80 μm , and was located centrally at the vessel base.

All experiments were performed in a water bath at $20\pm0.1^\circ\text{C}$ maintained with recirculating chiller (CTP-1000, TOKYO RIKAKIKAI, Tokyo, Japan). The pH and temperature meter (HM-21P with GST-2729C probe, TOA-DKK, Tokyo, Japan) and the dissolved oxygen (DO) meter (DO-24P with OE-270AA galvanic probe, DKK- TOA, Tokyo, Japan) were operated on line, as indicated in Fig. 1. The input air flow rate was set manually at 1 L min^{-1} by a mass flow meter (Kofloc, Kyoto, Japan) during measurement. A pressure regulator was used to maintain the inlet air pressure at 0.1 MPa for most air flow rates.

2.2 Oxygen transfer coefficient and α -factor determinations

The k_La in activated sludge was determined by the dynamic method [21]. Each activated sludge sample was centrifuged (3000 rpm (1650 g), 2 min) and concentrated

up to a 20 g L⁻¹ MLSS level before being diluted to the required concentration using the supernatant of centrifuged mixed liquor as diluent. MLSS, particle size distribution, mean particle size, SVI, μ_{ap} and density were determined for all these sludge samples, while μ_{ap} was determined for each supernatant, as described in section 2.5. When sludge samples were transferred to the stirred tank reactor, agitation (240 rpm) and aeration (1 L min⁻¹) were then started. As soon as the DO concentration reached equilibrium, aeration was stopped, and endogenous oxygen uptake rates (OUR_{en}) (mgO₂ g-MLSS⁻¹ h⁻¹) were measured. Each OUR_{en} was calculated from the linear rate of decrease of the dissolved oxygen concentration above the value at which the rate of oxygen utilization became dependent on DO (critical DO concentration) [22]. Before the DO had fallen below its critical concentration, aeration was restarted, the increasing DO concentration was measured over time and the $k_L a$ calculated. The mass transfer balance is given by the following equation:

$$\frac{dC_L}{dt} = k_L a (C_L^* - C_L) - OUR_{en} x \quad (1)$$

Where C_L is measured DO concentration, C_L^* is the saturation DO concentration, and x is MLSS concentration. Eq. 1 can be rearranged to Eq. 2.

$$C_L = -\frac{1}{k_L a} \left(\frac{dC_L}{dt} + OUR_{en} x \right) + C_L^* \quad (2)$$

The $k_L a$ was determined from the slope of the straight line obtained from a plot of C_L

against $dC_L/dt + OUR_{en} x$. The α -factor was calculated by dividing the mixed liquor $k_L a$ by the $k_L a$ of tap water used as control as in the following equation.

$$\alpha = \frac{k_L a_{\text{mixed liquor}}}{k_L a_{\text{tap water}}} \quad (3)$$

2.3 Agitation Reynolds number (Re) measurement

The agitation Re which measures the rheological properties of the mixed liquor was calculated according to Eq. 4.

$$Re = \frac{D_I^2 N \rho}{\mu_{ap}} \quad (4)$$

Where, D_I , N , ρ , and μ_{ap} are the diameter of impeller (m), rotation rate of impeller (s^{-1}), fluid density ($kg\ m^{-3}$), and apparent viscosity (Pa s).

2.4 Effect of adding flocculant on oxygen transfer coefficient determinations

The $k_L a$ values before and after flocculation of each activated sludge sample (Table 1) were determined as described in section 2.2. All mixed liquor samples were diluted to $10\ g\ L^{-1}$ MLSS level when the $k_L a$ was determined before adding flocculant. Agitation in the reactor was stopped and then 500 ml of supernatant was removed. The baffles in the reactor were removed and agitation (180 rpm) was then restarted upon addition of 500 ml (1% of MLSS) of the cationic dimethylaminoethyl acrylate

polyelectrolyte solution (ICM4204NG2, Ishigaki maintenance, Tokyo, Japan). After a rapid agitation period (180 rpm, 5 min), a slower agitation rate was imposed (50 rpm, 15 min). The k_La in flocculated activated sludge was then measured as before. The polyelectrolyte was dissolved in milliQ water with agitation for 24 h and the stock solution was prepared to 500 mg L⁻¹.

2.5 Analytical methods

The MLSS and SVI were measured according to standard methods [23]. Particle size distributions and mean particle sizes were measured with a laser diffraction/scattering particle size distribution analyzer LMS-24 (Seishin enterprise, Tokyo, Japan). The μ_{ap} of concentrated sludge suspensions and their supernatants were measured in triplicate using a rotary viscometer (TVC-7 with rotors no. 0 and no. 1, Toki sangyo, Tokyo, Japan) at a fixed rotating speed (20 rpm) and Ostwald viscometer, respectively. Activated sludge samples were incubated with agitation in a water bath at $20 \pm 0.1^\circ\text{C}$, and the μ_{ap} of sludge suspension was measured at the shear rate of 7.1 s⁻¹ (rotor no. 1) or 17.5 s⁻¹ (rotor no. 0) for 30 s when agitation was stopped. The shear rates were calculated according to Eq. 5.

$$\gamma = \frac{0.209N_r}{1 - \left(\frac{R_b}{R_c}\right)^2} \quad (5)$$

Where, γ , N_r , R_b , and R_c are the shear rate (s^{-1}), rotation rate of rotor (rpm), radius of rotor (m), and radius of cylinder (m). Viscosity of a 15 ml aliquot of the supernatant obtained after centrifugation (3000 rpm (1650 g), 3 min) was examined with an Ostwald viscometer in a water bath at $20 \pm 0.1^\circ\text{C}$.

3. Results and Discussion

3.1 Relationship between oxygen transfer rates and activated sludge sample characteristics

3.1.1 MLSS vs α -factor

The k_La of tap control sample was estimated in duplicate. The mean value (0.594) was then used for the calculation of the α -factor. The α -factor was compared with the MLSS concentrations ranging from 5-20 g L^{-1} . An increase in MLSS over a 5-20 mg-L^{-1} range resulted in either a linear or exponential decrease in the α -factor for all the examined activated sludge samples, as shown in Fig. 2. Such relationships between MLSS concentration and the α -factor (i.e. linear or exponential decreases) have been noted in other studies [4-5, 9-11]. However, these were undertaken in tanks of

different geometries using a range of different aeration devices, which would generate different energy dissipation rates and shear stresses [4]. The fall in oxygen transfer rates as MLSS concentration increased differed with each sludge sample. Here the α -factor of three sludge samples (WWTP A (Conv), WWTP A (A₂O), and WWTP B) showed almost identical trends. However, those for the lab scale reactor and WWTP C sludges were markedly different. Although both had a very similar α -factor value (approx 0.8) at 5 g L⁻¹ of MLSS concentration, the WWTP C sample value decreased sharply as MLSS concentrations increased and decreased to close to zero at 20 g L⁻¹ of MLSS concentration. This trend was also seen with the other WWTP sludge samples, although the lab reactor sludge showed a moderate α -factor decrease as MLSS concentrations increased, and its α -factor was close to 0.6 at 20 g L⁻¹ of MLSS concentration. These outcomes suggest that the oxygen transfer rate coefficient was affected not only by the aeration device but also by the characteristics of the activated sludge, since all the experiments discussed here were conducted using the same aeration device.

When two of the activated sludge samples from WWTP B were again analyzed after three months (Fig. 2) , their α -factors were very close at similar MLSS values (around 5 and 10 g L⁻¹), suggesting a high reproducibility of the oxygen transfer measurements in this study.

3.1.2 Correlation between activated sludge viscosity and α -factor

When α -factor values were compared to the corresponding μ_{ap} the following outcomes were seen. Fig. 3 shows the relationships between μ_{ap} at a shear rate of 7.1 s^{-1} and α -factor values for the samples shown in Fig. 2, for which the MLSS was adjusted as shown in Table 2. Some samples shown in Fig. 2 are not represented in Fig. 3 because their apparent viscosities were not measured. In Fig. 3, an increase in μ_{ap} for all examined activated sludge samples resulted in an exponential decrease in their α -factor values, which suggests that its value is determined by the μ_{ap} irrespective of the origin of the sample analysed. Gnder [11], Krampe and Krauth [9], and Rosenberger et al. [24] have all reported a correlation between α -factor and μ_{ap} . Furthermore, the relationships between them followed a similar exponential curve (i.e. $\alpha = \mu_{ap}^{-0.45}$ by Gnder [11]; $\alpha = \mu_{ap}^{-0.456}$ by Krampe and Krauth [9]) to that found here ($\alpha = 2.11 \mu_{ap}^{-0.384}$). This was despite them applying different reactor shear rates (i.e. Krampe and Krauth [9], 40 s^{-1} and Rosenberger et al. [24], 80 s^{-1}) to those used in our study (7.1 s^{-1}). In this present study, most α -factor values did not fit onto an exponential curve when plotted against MLSS values (Fig. 2) although most fitted an exponential curve when plotted against the determined μ_{ap} values (Fig. 3).

3.1.3 Influence of rheological properties on oxygen transfer rates

To investigate the influence of sludge rheological properties on oxygen transfer rates, the relationship between agitation Re and k_La was explored by increasing the rotation rate of the impeller (N) in the stirred tank from 50 min^{-1} to 240 min^{-1} . Fig. 4 shows the relationship between the N and k_La . As expected, an increase in impeller rotation rate resulted in an increase in k_La for all the examined activated sludge samples and the control sample. Fig. 5 shows the relationship between k_La and Re calculated from Eq. 4. It is clear that increasing Re results in an increase in k_La , and the relationship between them (shown with a black line) was determined from the following:

$$k_La = 0.0207Re^{0.416} \quad (6)$$

The relationship between the calculated (Eq. 6) and measured k_La values is shown in Fig. 6, suggesting that measured k_La values have an error of about 20%. Thus, Eq. 6 seems appropriate for predicting oxygen mass transfer coefficients in the stirred tank reactor.

3.2 Influence of adding organic polyelectrolytes on activated sludge characteristics and

233 *oxygen transfer rates*

234 Based on previously reported data, it is hypothesized that oxygen mass
235 transfer rates in activated sludge will increase if flocculant addition decreases the μ_{ap} .
236 Accordingly, k_La value of the activated sludge was compared before and after addition
237 of the cationic flocculant dimethylaminoethyl acrylate polyelectrolytes (Table 3). The
238 data show that the k_La values of the sludge samples obtained from WWTP A (Conv.),
239 WWTP A (A₂O), WWTP B, WWTP C, and WWTP D increased after polymer addition,
240 by 116%, 111%, 109%, 110%, and 113%, respectively. In contrast the k_La of lab scale
241 reactor sludge decreased, slightly to 95% of its original value. At a shear rate of 17.5 s⁻¹,
242 the μ_{ap} values of sludge samples obtained from WWTP C and WWTP D decreased after
243 flocculant addition, but not that of the lab reactor sludge. Thus, it seems that whether
244 flocculant addition improves the k_La in activated sludge depends on whether it reduces
245 correspondingly the μ_{ap} value.

246 Table 3 also shows the μ_{ap} values for the supernatant phase before and after
247 flocculant addition, where the differences between the respective values are much lower.
248 Therefore, the changes in μ_{ap} values seem to depend largely on changes to the physical
249 properties of the suspended solids phase, and not the liquid supernatant. In some
250 previous studies [15,25], a decrease of 13% in the oxygen transfer rate was reported for

activated sludge samples to which polyaluminium chloride (PAC) had been added.

Furthermore, the mixed liquor viscosity increased slightly, while the supernatant viscosity did not change [26]. Therefore, these data [15] also seem to suggest that changes to sludge particle size and shape might lead to a decrease in oxygen mass transfer rates following flocculant addition.

Many models have been used to determine suspension viscosity. Most of these essentially extend the work of Einstein on spheres, and use his equation [27]:

$$\mu_{ap} = (1 + 2.5\varphi)\mu_0 \quad (7)$$

where φ is the volume fraction of the solid phase in a solid–liquid mixture, and μ_0 is liquid viscosity with no suspended solids. Equation 7 means that μ_{ap} is a linear function of φ , although it was derived based on several theoretical assumptions. These included no effect on viscosity of particle size nor of particle position [28]. As shown in Table 3, the mean particle sizes of all activated sludge samples increased after flocculant addition, again as expected, while only the SVI of the lab reactor sludge increased. This suggests that all WWTP sludge flocs became denser after polyelectrolyte addition, while the lab reactor sludge flocs were more diffuse. As floc densities of the WWTP sludges increased, these volume fractions decreased, as did their μ_{ap} according to Eq. 7. On the other hand, as the floc density of lab reactor sludge decreased, the volume

fraction and μ_{ap} increased. The differences in flocculation between WWTP sludges and lab reactor sludge may depend on the pH of activated sludge. Gill and Herrington (1989) [29] have investigated the effect of pH on kaolin suspensions flocculated with cationic polyacrylamides, which were prepared by copolymerisation of acrylamide and dimethylaminoethyl acrylate quaternised with methyl chloride. They reported that large flocs and clear supernatants after flocculation were achievable at pH values below 7. In this present study, the pH values of WWTP sludges were around 7, while that of the lab reactor sludge was above 8 (Table 3), and only the lab reactor sludge seemed to show poor flocculation characteristics.

Moreover, Table 3 shows a slight decrease in the endogenous respiration rate of all the WWTPs sludge but not the lab reactor sludge, after flocculant addition. This result supports the view that flocs in the WWTP sludges were denser than they were in the lab reactor sludge, since respiration rates would depend on the extent of their contact area with oxygen. Also, some WWTP sludges showed a shift in their pH values from neutrality to mild acidity after flocculation (Table 3), while with the lab reactor sludge the pH was close to neutrality. Iversen *et al.* (2009) [15] reported that the decrease in endogenous oxygen mass transfer uptake rates after flocculation could be explained by a pH shift. Therefore, with high density flocs and a pH shift, bacterial respiration rate

would be affected by more than the apparent viscosity of activated sludge. Although exogenous oxygen uptake rates were not investigated in this study, as any decrease in bacterial respiration rate (i.e. endogenous and exogenous oxygen uptake rates) would lead to a lower treatment efficiency, further investigation on the influence of flocculation not only on oxygen mass transfer rates but also on bacterial respiration rates should be performed.

As mentioned in Eq. 7, an increase in φ of the solid phase in a solid–liquid mixture increases μ_{ap} , which reduces Re , as shown in Eq. 4. A low Re would maintain the flow in a reactor in a laminar state, thus ensuring the air bubbles remain large. Therefore, it can be hypothesized that any reduction of the interfacial area between the air bubbles and liquid phase would lead to a lower k_La value. Henkel *et al.* [30] have reported that an increase in φ itself may lead to the decrease of k_La . They quoted a review [31] and summarized several influence of φ on oxygen transfer rates as resulting from two phenomena; a reduction of turbulence in the bubble wake area, and suppression of the oxygen transfer from the bubble to the liquid phase. Further investigations should determine which of these phenomena is most responsible for the k_La changes recorded here.

Conclusions

- The α -factors are mainly influenced by not the MLSS concentration but the μ_{ap} values.
- There is an exponential correlation between the $k_L a$ of activated sludge and the Reynolds number of the stirred tank reactor. The correlation should not depend on the reactor scale because the Reynolds number is a dimensionless parameter which reflects liquid turbulence levels.
- Whether flocculant addition improved the $k_L a$ in activated sludge depended upon whether it reduced correspondingly the μ_{ap} value. Such a change in μ_{ap} depended largely not on the supernatant viscosity but on the volume fraction of suspended solids, measured as SVI, particle size and endogenous respiration rates.
- Any encouragement of high density floc formation may reduce the overall bacterial respiration rate in the mixed liquor.

Acknowledgment

The authors gratefully acknowledged Prof. Robert Seviour for his proofreading of the manuscript. The authors also express their gratitude to Mr. Shizuo Furukawa who helped to set up the stirred tank system. The Environmental Planning Bureau of

Yokohama City Government are acknowledged for their provision of activated sludge.

Dr. Kenzo Sugaya and Mr. Masayoshi Katayama are also acknowledged for their provision of polyelectrolytes ICM4204NG2.

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Figure captions

Fig. 1 Schematic diagram of the stirred tank system used in this study.

Fig. 2 Plots of decrease in α -factor values with increase of MLSS. The figure shows the data obtained in this present study and those from previous studies. Two of the activated sludge samples from WWTP B indicated by arrows were again analyzed after three months to check the reproducibility of the oxygen mass transfer measurements.

Fig. 3 Decreases in α -factor values with mixed liquor apparent viscosity (μ_{ap}). Each μ_{ap} represents the mean value of three measurements. The agitation rate of the stirred tank system was maintained at 240 rpm and the shear rate for the measurement of μ_{ap} was set at 7.1 s^{-1} .

Fig. 4 Increase in k_La values with increasing impeller rotation rate (N). Each legend shows sample origin, apparent viscosity, and MLSS in series. The apparent viscosities of lab scale reactor sludge ranged between 12.1-46.7 mPa s achieved by changing the MLSS (10-20 g L⁻¹).

Fig. 5 Correlation between k_La and agitation Reynolds number (Re).

Fig. 6 Correlation between measured k_La (k_La (Exp)) and calculated k_La (k_La (Cal)). The solid line illustrates the close agreement of k_La (Exp) and k_La (Cal) and the dashed lines show the error $\pm 20\%$.

Table 1 Summary of each WWTP and lab scale reactor, where activated sludge samples were collected.

Plant	Process	MLSS ^d (g L ⁻¹)	SVI ^d (ml g ⁻¹)	SRT ^d (day)
WWTP A	Conventional ^a	2.0	240	14
WWTP A	A ₂ O ^b	2.2	250	12
WWTP B	AOAO ^c	2.1	260	14
WWTP C	Conventional	2.3	240	11
WWTP D	Conventional	1.4	340	12
lab reactor	Aerobic batch	6.0	47.0	∞ ^e

^a Conventional activated sludge process operated with gentle aeration in the first few tanks

^b Anaerobic/Anoxic/Aerobic process

^c Anaerobic/Nitrification/Endogenous denitrification process

^d Annual average values in 2010 (Apr. 2010 to Mar. 2011)

^e No excess sludge had been withdrawn

Table 2 MLSS values for the samples shown in Fig. 3.

Activated sludge	MLSS (g L ⁻¹)
WWTP A (Conv.)	10
WWTP A (A ₂ O)	9.7
WWTP B	1.1, 3.2, 5.0, 9.9, and 10
WWTP C	5.4, 10, and 15
lab reactor	11, 18, and 22

Table 3 Activated sludge characteristics before and after flocculation.

Activated sludge	μ_{ap} (mPa s)	k_{La} (s ⁻¹)	μ_{ap} of supernatant (mPa s)	Mean particle diameter (µm)	MLSS (mg L ⁻¹)	SVI (mL g ⁻¹)	Endogenous respiration (mgO ₂ gMLSS ⁻¹ h ⁻¹)	pH ^b
WWTP A (Conv.)	127 ± 0.58	0.197	1.05 ± 1.2 × 10 ⁻³	135	10240	283	0.768	6.70
	43.2 ± 0.17	0.228	1.07 ± 1.3 × 10 ⁻³	141	10020	106	0.610	6.76
WWTP A (A ₂ O)	84.4 ± 0.35 ^a	0.239	1.02 ± 3.6 × 10 ⁻³	70.8	9580	291	0.621	7.05
	22.0 ± 0.25	0.265	0.984 ± 8.2 × 10 ⁻³	97.9	9580	83.3	0.547	6.87
WWTP B	114 ± 0.58 ^a	0.228	1.06 ± 3.5 × 10 ⁻³	146	9840	282	0.579	7.09
	45.5 ± 0.17	0.249	1.06 ± 2.6 × 10 ⁻³	157	9760	130	0.535	6.89
WWTP C	20.4 ± 0.21 ^a	0.275	1.05 ± 7.6 × 10 ⁻³	149	10080	84.4	0.615	6.96
	9.7 ± 0.44	0.303	1.03 ± 1.9 × 10 ⁻³	177	9480	62.5	0.603	6.59
WWTP D	52.73 ± 0.68	0.248	1.05 ± 3.4 × 10 ⁻³	95.1	10840	260	0.529	7.35
	18.60 ± 0.17	0.281	1.01 ± 6.0 × 10 ⁻³	145	10080	63.5	0.482	7.17
lab reactor	6.1 ± 0.060	0.420	1.01 ± 3.2 × 10 ⁻³	75.0	9300	46.9	0.0661	8.32
	13.5 ± 0.10	0.399	1.03 ± 1.4 × 10 ⁻³	93.5	9540	58.3	0.0990	8.11

Upper stand shows the values before flocculation and lower stand after flocculation. The μ_{ap} and μ_{ap} of supernatant were measured in triplicate; average values ± standard deviations are shown.

^a These three μ_{ap} values were measured at the shear rate of 7.1 s⁻¹ although the other μ_{ap} values were measured at the shear rate of 17.5 s⁻¹.

^b The pH values were measured at the beginning (0 min) of endogenous respiration measurement.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6