



CHAPTER 2

BACKGROUNDS AND LITERATURE REVIEW

2.1 Oxygen Transfer

Oxygen transfer, the process by which oxygen is transferred from the gaseous to the liquid phase, is a vital part of a number of wastewater-treatment processes. Oxygen transfer is controlled by the partial pressure of oxygen in the atmosphere (0.21 atm) and the corresponding equilibrium concentration in water (approximately 10 mg/L). According to Henry's Law, the equilibrium concentration of oxygen in water is proportional to the partial pressure of oxygen in the atmosphere (Webber, 2001).

At high levels of supersaturation dissolved gas will form microbubbles that eventually coalesce, rise, and burst at the water surface. The bubbles provide a very efficient transfer of supersaturated dissolved gas to the gaseous phase, a process that can be observed when the partial pressure of carbon dioxide is decreased by opening a carbonated beverage. Bubble formation by supersaturated gasses also occurs in the environment when cold water in equilibrium with the atmosphere is warmed rapidly. The equilibrium dissolved oxygen concentration is a function of temperature and as the water is warmed the equilibrium concentration decreases (Webber, 2001).

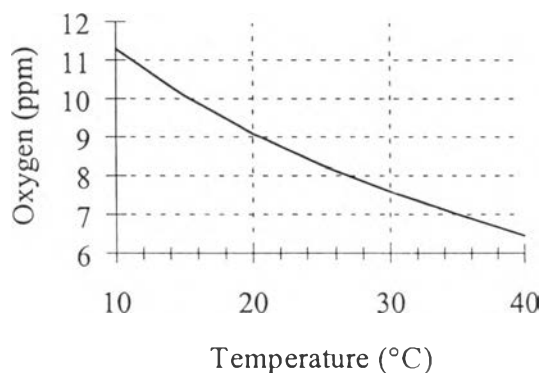


Figure 2.1 Dissolved oxygen concentrations in equilibrium with the atmosphere as a function of water temperature (Webber, 2001).

2.1.1 Oxygen Transfer Rate

Stenstrom *et al.*, (1981) proposed that estimating the oxygen transfer rate are usually made by determining the volumetric oxygen transfer coefficient and equilibrium procedures have oxygen concentration from a non-steady state reaeration test. The volumetric mass transfer coefficient and equilibrium dissolved oxygen (DO) concentration are usually estimated by fitting the concentration versus time data to the two-film model, as follows:

$$\frac{dDO}{dt} = K_L a (DO^*s - DO) \quad (2.1)$$

in which DO = DO concentration, in milligrams per liter;

DO*s = saturation DO concentration, in milligrams per liter, at equilibrium;

$K_L a$ = volumetric oxygen transfer coefficient, t^{-1} ; and t = time.

The exponential method is used in this study because the sum of square errors of this method is less and the residuals (the different between the expected and measured value) are more uniform than other methods. Truncation of data when DO approaches DO*s is not required. The other reasons are DO*s can be estimated from the data, which means no error is introduced and the precision of the estimates for DO*s and $K_L a$ is much greater than the other methods

This exponential equation integrated from Eq. 2.1, as follows:

$$DO = DO^*s - (DO^*s - DO_0) e^{(-K_L a t)} \quad (2.2)$$

in which DO_0 = DO concentration when t = 0

2.1.2 Effect of Temperature on Oxygen Transfer

In aeration, oxygen transfer coefficients are influenced by temperature due to the effect on the diffusivity and viscosity.

$$K_L a = K_L a_{20} \cdot \theta^{T-20} \quad (2.3)$$

Reported values of θ range from 1.012 to 1.04. The most reliable estimates are 1.020 for diffused aeration and 1.028 for surface aeration. The ASCE standard (1993) uses 1.024, and this value must be used when doing a standard test.

2.2 Aeration System

There are several types of aeration system used for wastewater treatment. The systems used depend on the function to be performed, type and geometry of the reactor, and cost to install and operate the system (Metcalf & Eddy, 2003). The two most common aeration systems are surface and subsurface. In a surface system, air is introduced from the atmosphere agitating the wastewater by various means (e.g., propellers, or blades). For a subsurface, air is introduced by diffuser or other devices submerged in the wastewater. Turbine aeration system is a submerged form of aeration in which air is discharged from a sparge ring beneath a rotating impeller. The action of the impeller forces flow downward and shears the bubbles (making them smaller with higher surface renewal). Air flow, diameter of turbine and speed of motor all influence $K_L a$ (Stenstrom, 2001).

The presence of surfactant in wastewater is the one of the major problems for an aeration system. Unsuitable estimation of the oxygen transfer rate (OTR) also caused the process efficiency and the cost of energy consumption problems. The optimum oxygen transfer rate should be studied by using oxygen transfer coefficient ($K_L a$) to find the best efficiency with suitable power input. Financial cost concerns would then be reduced.

2.2.1 Turbine Aeration

In turbine aeration, air is discharged from a sparge ring beneath a rotating impeller. The action of the impeller forces flow downward, shearing the bubbles (making them smaller with higher surface renewal). Air flow, diameter and speed all influence $K_L a$ (Boyle et al., 1989).

Equation developed

$$N = CRG_s d_t^{(C_s - C)} \quad (2.4)$$

and $HP = Cd_t R$ Power drawn by turbine (2.5)

where,

N	=	transfer rate, lbs O ₂ /hr/aeration unit
C _s	=	saturated O ₂ concentration in waste
G _s	=	air flow, SCFM/aeration unit
R	=	impeller peripheral speed, rev
d _t	=	impeller diameter, m
HP	=	horse power

Optimal conditions for most turbines exist when the power required to compress the air that is discharged below the turbine impeller equals the impeller's power.

2.2.2 Aerator Performance

Mechanical aerators are rated in terms of their oxygen transfer rate expressed as kilograms of oxygen per kilowatt-hour (pounds of oxygen per horsepower-hour) at standard conditions. Standard conditions exist when the temperature is 20 °C, the dissolved oxygen is 0.0 mg/L, and the test liquid is tap water. Testing and rating are normally done under non-steady-state conditions using fresh water, deaerated with sodium sulfite. Commercial-size surface aeration range in efficiency from 1.20 to 2.4 kg O₂/kW.h (2 to 4 lb O₂/hp.h) (Metcalf & Eddy, 2003).

2.3 Surfactants

The word surfactant does not appear in most dictionaries. This is because it is not only a technical term, but also a diminutive form of the phrase SURFace ACTive AgeNT. Surfactants, or surface active agents, are important ingredients in washing agents, cleaning agents and soaps. A surfactant molecule consists of a hydrophilic part and a hydrophobic part. As a function of their electric loading, surfactants can be divided into anionic, nonionic, cationic, and amphoteric surfactants. Surfactants are slightly soluble in water and cause forming in wastewater treatment plants and in the surface waters into which the waste effluent is discharged (Metcalf & Eddy, 2003). Mostly, an anionic surfactant type is used and presented in wastewater. The concentrations of the other types of surfactants are very low and therefore of no importance with regard to the oxygen transfer process (Wagner M. *et al.*, 1996).

2.3.1 Effect of Surfactants on Oxygen Transfer

Surfactants have polar and non-polar parts of the molecule. The simplest has a polar end, often charged, and a non polar end, such as a hydrocarbon. The most common surfactant is soap, which was originally manufactured by mixing animal fat and lye (sodium hydroxide). The result is a surfactant with a negatively charged end (the sodium is released to solution as the balancing cation). Hydrogen bonding among water molecules will gradually force the surfactant's non polar end to the surface. This happens because the polar ends of the water molecules attract each other, and squeeze the surfactant out of the way. The result is the surfactant at the interface (e.g., the air bubble surrounded by water) with the polar or charge end in the water and the non polar end protruding into the bubble. The net effect is to reduce oxygen transfer in the area around the bubble by reducing molecular diffusion of oxygen. (Webber, 2001).

The time required for adsorption varies with the surfactant type. Small surfactants such as acetic acid adsorb quickly. The time to reach equilibrium depends upon many different properties, but is inversely proportional to the molecular weight of the surfactant.

Stenstrom (2001) summarized four basic effects of surface active agents (SAA) on gas transfer:

1. The adsorbed film, which may partially or totally cover the water surface and thus act as an insulating membrane separating the gas and the aqueous phase. An oil sheen is an example. This effect increases resistance to gas transfer.

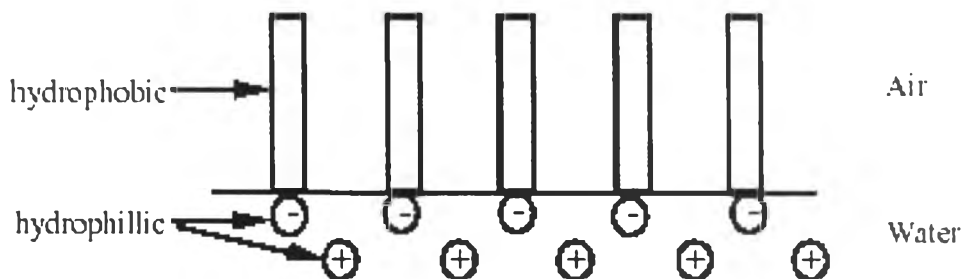


Figure 2.2 Adsorption mechanisms (Stenstrom Lecture Note, 2001)

2. Water in a pure state generally consists of aggregates of 4 to 8 molecules of water that are in a state of dynamic equilibrium. When SAA molecules are introduced to the pure water, they tend to affect the water structure by stabilizing the more ordered arrangements. The SAA molecules anchored to the water surface with their hydrophilic ends will act like magnet heads that immobilize several layers of crystalline water structures and attract a blanket of counter ions. This surface hydration layer, may extend several thousand angstroms into the aqueous phase, which eliminates random surface motion (i.e., encourages surface stagnation).

3. Surface active agents can influence bubble dynamics. During the bubble rise the SAA film adsorbed on the bubble wall will be driven to the far end of the bubble where it condenses, forming a solid cap. As a result a surface force will be set in the direction of the front end of the bubble, opposing the liquid drag forces which may cause a retardation in the velocity of bubble rise.

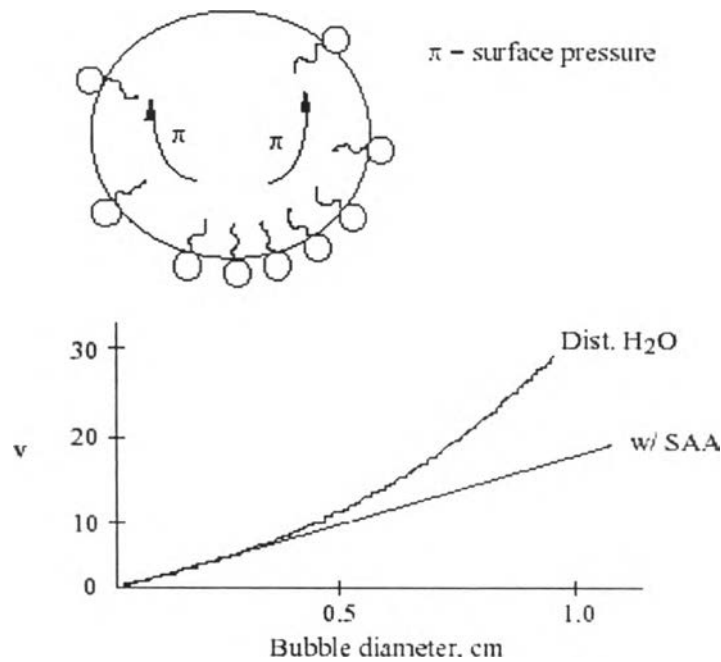


Figure 2.3 Relationship between velocity of bubble rise and bubble diameter (Stenstrom Lecture Note, 2001)

4. Diffusers produce smaller bubbles in the presence of surfactants. Larger bubbles with $N_{Re} > 800$ undergo fragmentation in the presence of SAA. The smaller bubbles have greater surface area per unit volume of gas supplied, which increases gas transfer rate.

2.4 Deoxygenation

This test is the basis for clean water testing which is used for most performance testing of aeration equipment. The test is performed and the data are analyzed based upon one of the previously described equations. To perform the test, one usually supplies a deoxygenating chemical to remove the oxygen. Aeration is provided and the rates of transfer are calculated from the rate at which the water can be reaerated. The graph below shows the DO concentration during a test. The sulfite is rapidly added and the DO plunges quite rapidly to zero or near zero. After some period, the DO returns and the concentration gradually increases to the equilibrium value.

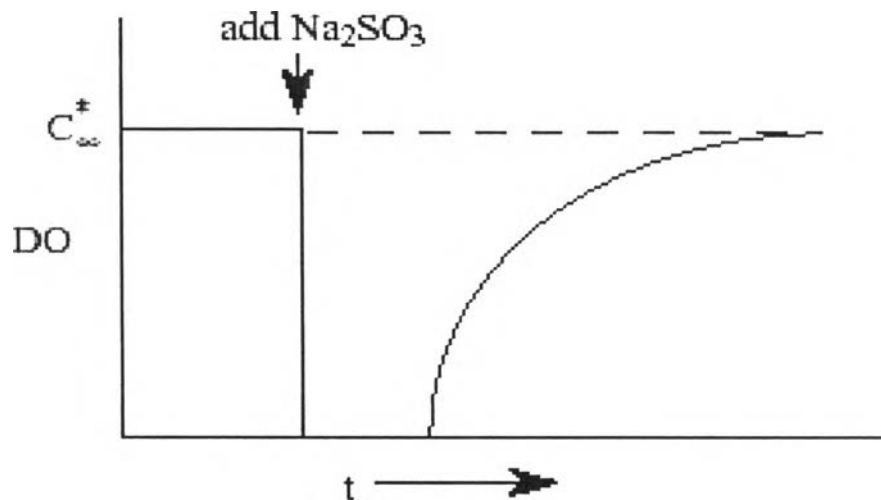


Figure 2.4 DO concentration during a test (Stenstrom Lecture Note, 2001)

To perform a nonsteady-state reaeration test, one adds sodium sulfite to deaerate or strip the water of DO, as follows:



The reaction is very fast and is catalyzed by cobalt ion. Cobalt is usually added as Cobalt-Chloride. The reaction is so rapid that measurable DO and sulfite are present at the same time.

Sulfite is usually added by first dissolving the sulfite in water and then pouring the water into the reactor. This avoids clumps of sulfite that dissolve too slowly. A saturated sulfite solution contains 2.23 lb/gal at 20 °C and 3.00 lb/gal at 30 °C. Add 7.88 mg/L sulfite per 1 mg/L DO plus some excess to insure that all the DO is removed. For low rate aeration systems, usually only 25% extra is added. For very large systems, as much as 100% excess is added.

2.5 Power Input

2.5.1 Energy Dissipation in Mixing

Metcalf & Eddy (1997) stated that the power input per unit volume of liquid can be used as a rough measure of mixing effectiveness, based on the reasoning that more input power creates greater turbulence, and greater turbulence leads to better mixing. The study of the establishment and effect of velocity gradients in coagulation tanks of various types and developed the following equations that can be used for the design and operation of mixing systems.

$$G = \sqrt{\frac{P}{\mu V}} \quad (2.7)$$

where:

- G = mean velocity gradient, 1/s
- P = power requirement, W
- μ = dynamic viscosity, $\text{N} \cdot \text{s}/\text{m}^2$
- V = volume, m^3

2.5.2 Power Requirement for Mixing

The power requirement for mixing using propeller was described in this research. Using propeller for mixing in wastewater processes usually occurs in the regime of turbulent flow in which inertial force predominate. As a general rule, the higher the velocity and the greater the turbulence, the more efficient the mixing. On the basis of inertial and viscous force, the mathematical relationships have been developed for power requirements for turbulent conditions as follow:

$$\text{Turbulent:} \quad P = k\rho n^3 D^5 \quad (2.8)$$

where:

- P = power requirement, W
- k = constant 6.30 for turbine, 6 flat blades (Metcalf & Eddy, 1991)
- ρ = mass density of fluid, kg/m^3
- D = diameter of impeller, m
- N = revolutions per second, rev/s

For turbulent range, it is assumed that vortex conditions have been eliminated by four baffles at the tank wall, each 10 percent of the tank diameter (Metcalf & Eddy, 2003). The Reynolds number is given by

$$N_R = \frac{D^2 n \rho}{\mu} \quad (2.9)$$

where:

- D = diameter of impeller, m
- n = rev/s
- ρ = mass density of fluid, kg/m³
- μ = dynamic viscosity, N · s/m²

Vortexing, or mass swirling of the liquid, must be restricted with all types of impellers. Vortexing causes a reduction in the difference between the fluid velocity and the impeller velocity and thereby decreases the effectiveness of mixing. The usual method in circular tanks is to install four or more vertical baffles extending approximately one-tenth the diameter out from the wall. These effectively break up the mass rotary motion and promote vertical mixing. Concrete mixing tanks may be square and the baffles may be omitted (Metcalf & Eddy, 1997).

2.6 Literature review

Stenstrom (1978) noted that the equations for oxygen transfer and parameter estimation techniques used today include the differential technique, the log deficit method, and the exponential method. The overall analysis of three methods for parameter estimation suggests that the exponential method is the most suitable for estimating the oxygen transfer. As a result, the exponential and differential technique tend to produce estimates which have larger residuals in the early states of the non steady state test, while the log deficit method produces estimates which have larger residues toward the end of the test. The log deficit technique needs data truncation while the other two methods do not require it. The differential technique is the easiest to perform but suffers from large variability in the data, due to the magnifying effects of the differentiation. Therefore, the exponential method of parameter estimation provides the most precise estimates of $K_L a$ and DO^*s .

Stenstrom and Hwang (1980) observed that alpha factor which is normally used to convert clean water oxygen transfer rates to field transfer rates is at best a semiquantitative tool. It is obvious that the alpha factor for identical fluids can vary by 100% for different aeration devices and power level. Using this widely varying range of alpha factors, it would be impossible to adequately specify and design an aeration system. It appears that alpha testing should be more rigorously defined and standard procedures should be developed. Two important ramifications of this work for such a standard procedure are the specifications of aeration device and power level.

Stenstrom, Brown, and Hwang (1981) found that the most common procedure for estimating the oxygen transfer rate of an aeration system is to estimate the clean water rate and then translate that rate to field conditions with alpha, beta, and theta correction factors. Estimates of the clean water transfer rate are usually made by determining the volumetric oxygen transfer coefficient and equilibrium oxygen concentration from a non steady state reaeration test. They demonstrated the use of the exponential parameter estimation technique using two nonlinear programming techniques, the complex method and the linearization technique. Both techniques can accommodate an adequate number of observations. These eliminate the need for estimating C^* s from handbook or depth/correction methods, and also eliminate the data truncation when the DO concentration approaches saturation.

Masutani and Stenstrom (1991) noted the correlation of the volumetric mass transfer coefficient (K_La) and the liquid film coefficient (K_L) with dynamic surface tension (DST) in the presence of a surface active agent. When the surfactant concentration increased, the time of bubble formation and bubble volume decreased. The larger decrease in K_La occurs with higher surfactant concentrations. Repeated unsteady state surfactant aeration testing indicated K_La increased as the number of experiments on the sample solution increased. An antifoam agent decreased K_La value. As a result, K_La can be estimated from aeration parameters, surfactant concentration, and the DST value.

Masutani and Stenstrom (1991) found that oxygen transfer rates decrease in the presence of surface active agents (surfactants) such as detergents or soaps. Surfactants tend to 1) stabilize the interface, making the gas/liquid interface more rigid; 2) decrease surface renewal; 3) increase interfacial viscosity. When surfactant concentration increases, the time of bubble formation and bubble volume decreases. The adsorption of the surfactants onto the gas/liquid interface decreases the available surface area for molecular diffusion, and forms a hydration layer at the surface, resulting in higher surface viscosity and increased thickness of the surface layer, which increases resistance to oxygen transfer.

Wagner and Johannes (1996) found that the oxygen transfer efficient is reduced in all surfactant solutions in comparison to clean water. The influence of hardness and surfactant concentration is very high. With regard to the effect of surfactants on the bubble size, it is evident, that the specific interfacial area increases in all surfactant solutions. Anionic surfactants produce higher values than others. There is no relationship between the surface tension and the alpha value.

Wagner and Popel (1996) studied the effect of surfactant on the oxygen transfer rate in a fine-bubble aeration system and found that the volumetric mass-transfer coefficient decreased in the presence of surfactant.