

The Effect of Sodium Sulfite and Cobalt Chloride on the Oxygen Transfer Coefficient

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ABSTRACT

An experiment was conducted in an aeration system made from 2000 mL Erlenmeyer Flask to investigate the effect of sodium sulfite with cobalt chloride and the sparging nitrogen gas on the measurement of the oxygen transfer coefficient. Twice the theoretical quantity of sodium sulfite that is required to react with dissolved oxygen, or nitrogen sparging at a rate equivalent to that of air used during the aeration process, was used to deoxygenate the water. The results obtained from the study were consistent and repeatable and showed no significant differences in the values of the oxygen transfer coefficient obtained by the two methods.

Index Entries: Aeration; oxidation ditch; sodium sulfite; cobalt chloride; nitrogen; deoxygenation.

INTRODUCTION

Increased interest in the use of aerobic methods of livestock waste treatment has initiated a proliferation of aeration devices to accomplish the desired treatment. The wide variety of mechanical aeration devices has caused producers, manufacturers, and researchers to be curious as to the suitability of these devices for animal waste treatment.

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The main functions of any aeration device are: to supply sufficient quantity of oxygen to the liquid medium, to circulate the liquid in order to keep solids in suspension, and to distribute the oxygenated liquid through the liquid body. The oxidation ditch system has been successfully used for treating animal waste because of these criteria (1-3). The ditch essentially consists of a closed loop, open channel (Fig. 1) in which liquid circulation and oxygen input are maintained by a mechanical device. The disk aeration described by Ghaly (1) and Drews et al. (4) is an alternative to the brush and paddle wheel rotors that are traditionally used in oxidation ditches.

To ensure adequate aeration in an aerobic unit treating animal waste, the aeration system must be properly specified and tested. This has been made possible by the development of testing methods over a period of years. One of the real contributions in understanding aeration systems was made by Gaden (5) who established a single mass transfer coefficient that simplified the mathematical evaluation. He also proposed the use of nitrogen gas or sodium sulfite for deoxygenating the water and the determination of oxygen transfer characteristics from the reaeration date, a method that had been accepted as the basic aeration test in clear water.

Ghaly and Kok (6) and Ghaly (1) found it impossible to use nitrogen gas to completely deoxygenate the water in the oxidation ditch system because of the shape of the system and the difficulty of achieving adequate mixing of the nitrogen gas into liquid phase. Although the sodium sulfite method was questioned by Kalinske et al. (7), who claimed that it produced high transfer values, Ghaly (1) found it to be very effective in the oxidation ditch. Since the sodium sulfite method with cobalt chloride is believed to be the most suitable procedure for evaluating the oxidation ditch, this study was designed to determine whether there would be any significant differences between the oxygen transfer coefficient values obtained using the two procedures: nitrogen gas vs sodium sulfite.

THEORETICAL CONSIDERATIONS

Although several procedures have been used to estimate the overall volumetric oxygen transfer coefficient (K_La) of aeration devices, the unsteady state aeration procedure with sulfite oxidation, developed by W. E. Adeney in 1932 and later proposed by Gaden (5), has been generally adopted as the standard. The test involves chemical removal of dissolved oxygen from water by the addition of sodium sulfite (Na_2SO_3) with cobalt chloride ($\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$) added as a catalyst. The subsequent increase in oxygen concentration is measured during the aeration period by means of the Winkler Test or by the use of a dissolved oxygen probe. The basic aeration equation employed in aeration equipment evaluation is as follows:

$$\frac{dC}{dt} = K_La (C_s - C) \quad (1)$$

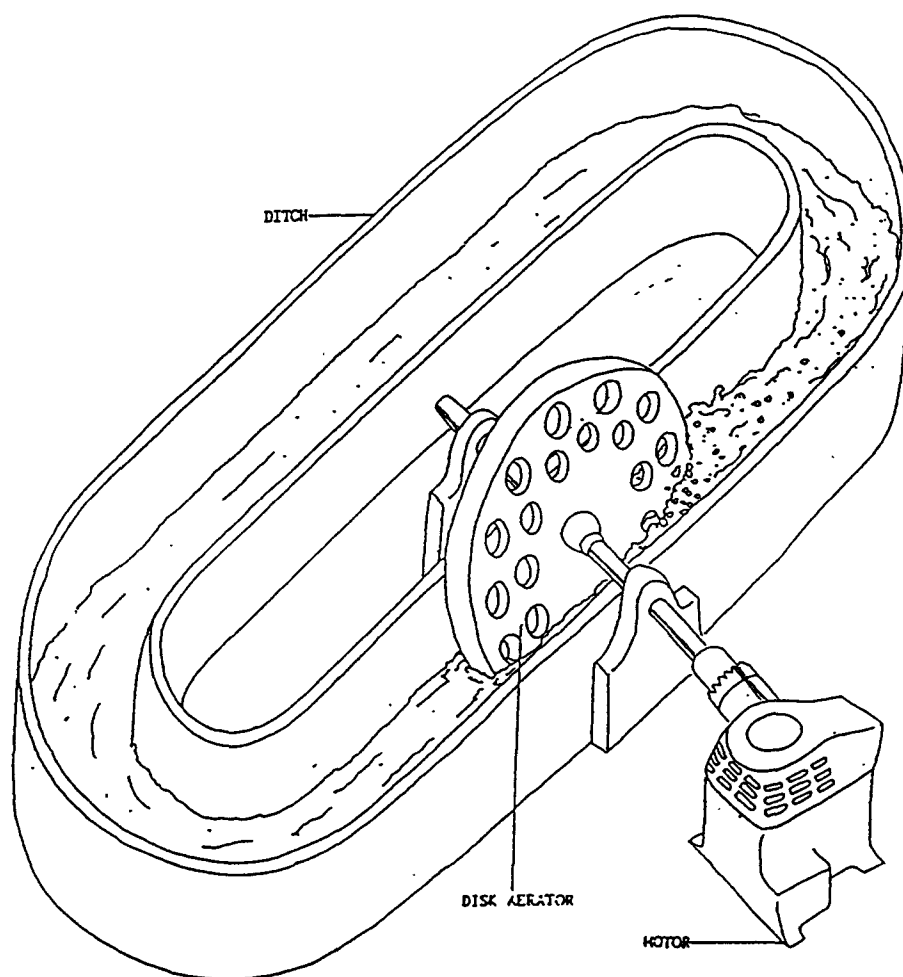


Fig. 1. Oxidation ditch.

where

$\frac{dC}{dt}$ is the derivative of oxygen concentration with time (mg/L/h).

$K_L a$ is the overall oxygen transfer coefficient (h^{-1}).

C_s is the solubility of oxygen in water, in contact with air (mg/L).

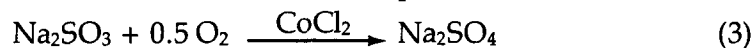
C is the dissolved oxygen concentration in water (mg/L).

At time $T=0$, $C=0$, and equation 1 on integration yields

$$C = C_s (1 - \exp(-K_L a t)) \quad (2)$$

This equation represents a curve of the rise in oxygen concentration (C) in a body of water with respect to time. Plotting the natural log of $(C_s - C)$ against (t) results in a straight line with a slope equal to the negative value of $K_L a$.

The amount of sodium sulfite that should be added to the reactor is very important. The stoichiometric relationship is as follows



Theoretically, 7.9 mg/L sodium sulfite is needed for each mg/L of dissolved oxygen (DO). Nonetheless, there is great disagreement in the literature regarding the qualities of chemicals required to deoxygenate a body of water and the effect of these chemicals on the value of K_{La} (1,6–10). However, because it is necessary to mix the sodium sulfite throughout the aeration tank before the test starts, oxidation of some sulfite occurs during the mixing period. Therefore, the addition of approximately 1.5–2.0 times the theoretical quantity of sodium sulfite has been suggested by Stukenberg et al. (8) as being necessary to deaerate the basin.

OBJECTIVES

The aim of this study was to investigate the effect of concentrations of the chemicals (0.2 mg/L of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ and 15.8 mg/L of Na_2SO_3) that were proposed by Stukenberg et al. (8) on the measurement of the oxygen transfer coefficient as compared to nitrogen gas.

EXPERIMENTAL APPARATUS

This experiment was conducted in a 2000 mL Erlenmeyer flask. A general purpose filtering funnel (Kimble 28950 No. 10-322E) was used to gradually add sodium sulfite and cobalt chloride solutions to the aeration flask. The funnel was connected to the flask by means of Tygon and glass tubes. A magnetic stirrer (Canlab No. S8290) with a magnetic stirring bar of 9.5 mm diameter and 51 mm length (Canlab Magnetic Spinbar No. S8306-156) were used to mix the air (or N_2) into the liquid phase. The magnetic stirrer operated at 500 rpm.

The air and nitrogen gases used in this experiment were obtained in cylinders from Canadian Liquid Air Ltd. A multi-stage gas pressure regulator was connected to each cylinder in order to control the flow rate from it (Fisher No. 10-572X was used for air; Fisher No. 10-5720 was used for N_2). A general purpose laboratory flowmeter (Lab Crest Series 100 Century Flowmeter No. S1 2123) was used to measure and control the air and nitrogen flow rates.

The barometric pressure was measured by a mercury barometer (Fisher 2-383). The dissolved oxygen was measured by a polarographic electrode (Beckman 39532 O_2 Sensor) connected to a dissolved oxygen meter (Beckman Field Oxygen Analyzer Model 1008). The signal from the dissolved oxygen meter was recorded continuously on a servo recorder (Health Model Eu-20B). The liquid temperature was measured by a thermistor sensor (Beckman Model 39590). A complete set-up of the apparatus is schematically presented in Fig. 2.

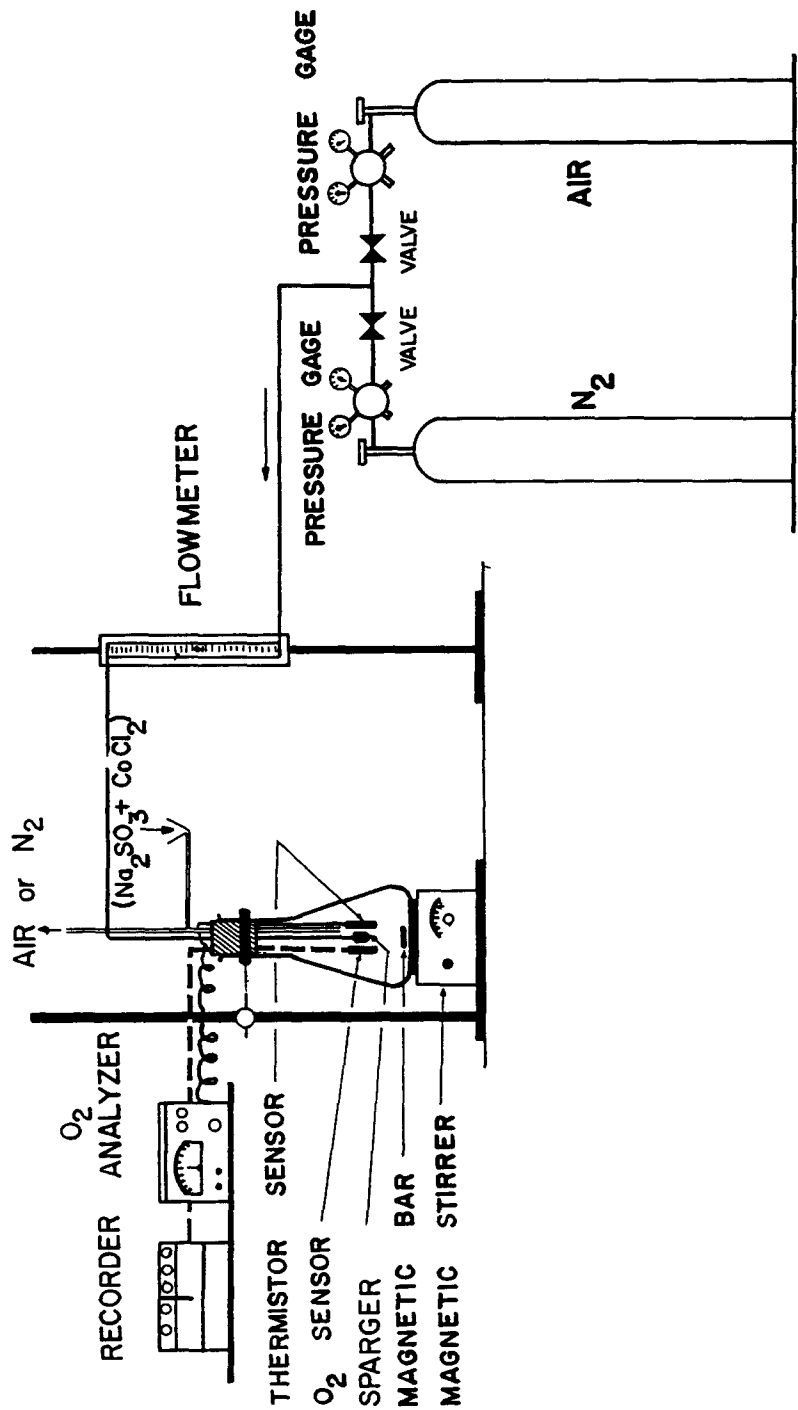


Fig. 2. Schematic diagram of the apparatus used to study the effects of sodium sulfite and cobalt chloride on the oxygen transfer coefficient.

EXPERIMENTAL PROCEDURE

A number of experiments were performed to determine the K_La value in the aeration flask. During each experimental run, the flask contents were aerated, deoxygenated, and then aerated again. The unsteady state method with sulfite oxidation (or nitrogen sparging) was used in this study.

Initially, the flask was cleaned thoroughly, with tap water and then flushed several times with distilled-deionized water before each run. Then 500 mL of deionized water were added to the flask. The air valve was opened and the air flow rate adjusted to the required value ($70 \text{ cm}^3/\text{sec}$). The dissolved oxygen meter, recorder, and magnetic stirrer were started simultaneously. The liquid temperature and room barometric pressure were then recorded.

When oxygen saturation concentration (C_s) had been reached, the air valve was closed and the magnetic stirrer shut off. Either one of the following procedures was then performed

1. In the sodium sulfite oxidation experiments, 0.7 mL of 0.100M Na_2SO_3 solution and 0.7 mL of 0.001M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution were added. These solutions were distributed throughout the water body by the magnetic stirring bar at a low magnetic stirrer speed (100 rpm), just enough to mix the flask contents.
2. In the nitrogen sparging experiments, the nitrogen valve was opened and the flow rate was adjusted to $70 \text{ cm}^3/\text{sec}$. The magnetic stirrer speed, used for mixing the nitrogen into the body of water, was equal to that used for aeration.

When the water was completely deoxygenated (either by SO_3 or N_2), the same aeration procedure was again performed and the dissolved oxygen concentration (C) was allowed to increase until it reached the saturation concentration (C_s).

RESULTS

During a typical experiment, C remained at zero until the excess sodium sulfite has been oxidized, rose rapidly at the beginning and then slowly approached its saturation value again. A typical recorded curve of the entire process of saturation-deoxygenation-reaeration is shown in Fig. 3. The data from the aeration curve were plotted on semilogarithmic paper to determine K_La . An example is shown in Fig 4.

The laboratory temperature and pressure varied during the course of experiment from 19 to 24°C and from 100 to 103 kPa, respectively. Since the concentration of oxygen in liquid is affected by the atmospheric pressure, the following equation, proposed by the American Public Health Association (APHA) (11), was used for pressure adjustment.

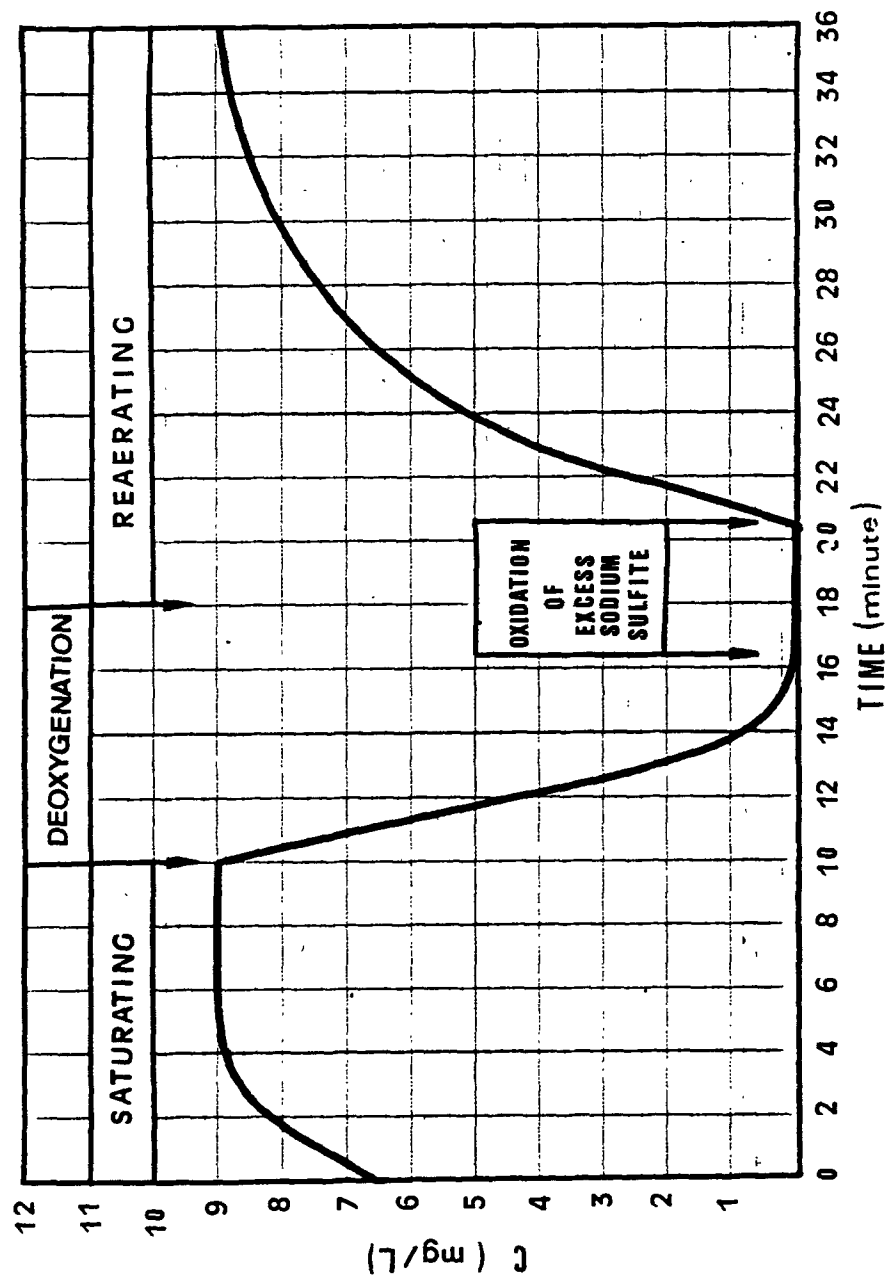


Fig. 3. The oxygen concentration curve obtained during a typical experimental run.

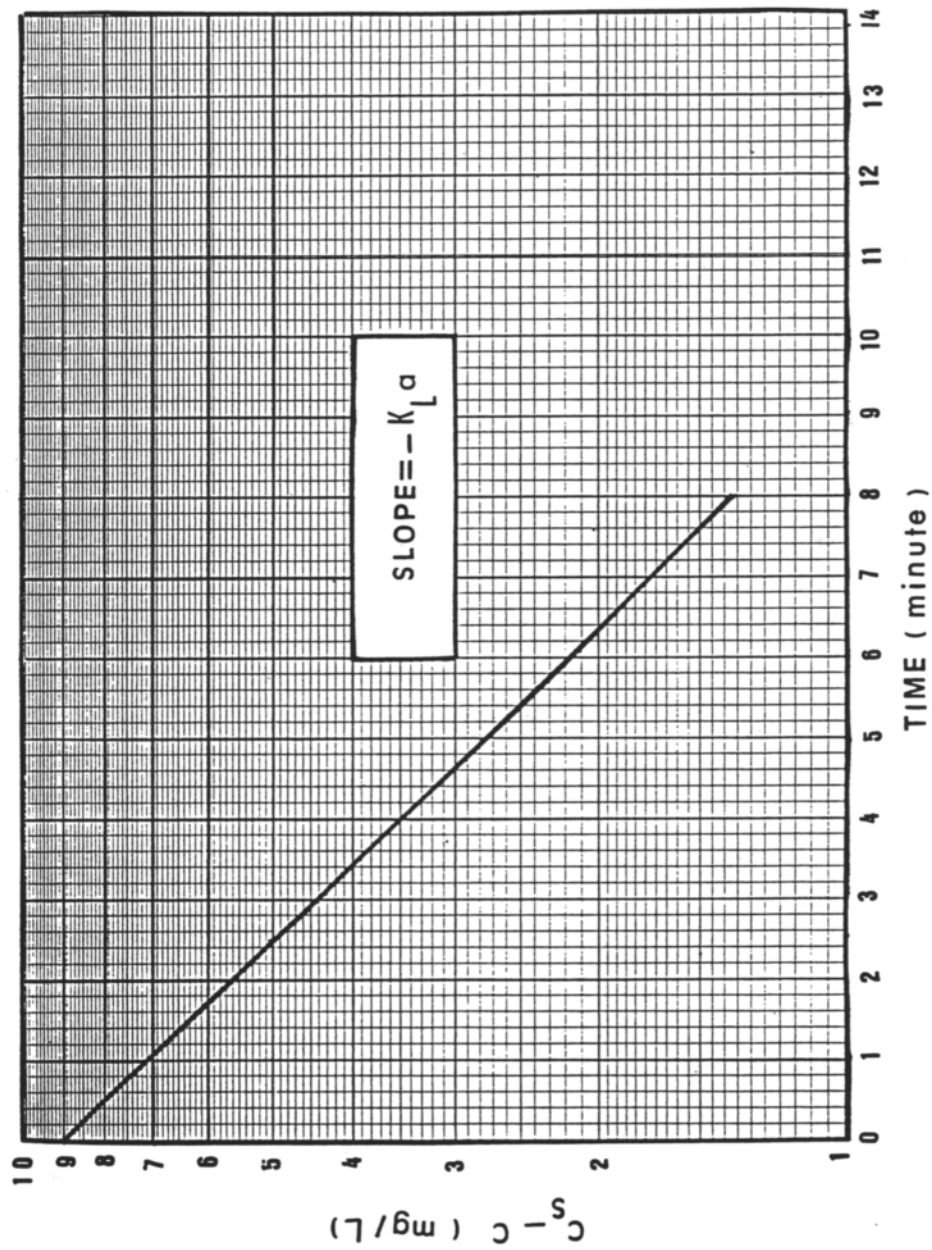


Fig. 4. Determination of $K_L a$.

$$C_{SP} = C_S \left(\frac{P_{ab}}{P_{at}} \right) \quad (4)$$

where

C_{SP} is the concentration of oxygen in water at barometric pressure P (g/L).

P_{ab} is the absolute laboratory barometric pressure (kPa).

P_{at} is the standard atmospheric pressure (kPa).

It is also clear from Eq. (1) that any error in the measured value of C_s (owing to temperature change) will affect the calculated value of K_{La} . According to Loehr (2), the changes in liquid temperature will affect the liquid mass transfer coefficient and the size of the bubbles generated in the system. The overall effect of temperature on K_{La} is described by the following equation

$$K_{La}(20) = K_{La}(T) 1.024^{(20-T)} \quad (5)$$

where

$K_{La(T)}$ is the overall volumetric oxygen transfer coefficient at a given temperature T ($^{\circ}\text{C}$) (h^{-1}).

$K_{La(20)}$ is the overall volumetric oxygen transfer coefficient at 20°C (h^{-1}) is the temperature ($^{\circ}\text{C}$).

Therefore, in order to standardize results, K_{La} values obtained under laboratory conditions were converted to their equivalent values at 20°C using Eq. 5. This left K_{La} exclusively a function of the interaction between the aeration device and aeration basin.

The standardized results of these experiments are reported in Table 1. The data were statistically analyzed to test for differences in K_{La} owing to the effect of the two treatments (deoxygenation of water by N_2 and SO_3). Simple statistics of the treatments are shown in Table 2. The weighted

Table 1
Values of K_{La} Obtained in Deionized Water After Deoxygenation
by Nitrogen Gas and Sodium Sulfite

Observations	$K_{La} (\text{min}^{-1})^a$	
	N_2	Na_2SO_3
1	0.3057	0.3090
2	0.3102	0.3243
3	0.3344	0.3105
4	0.3292	0.3331
5	0.3170	0.3147
Mean	0.3193	0.3183

^aConverted to equivalent at the barometric pressure of 101.3 kPa and room temperature of 20°C .

Table 2
Simple Statistics of the Two Treatments (N₂ and Na₂SO₃)

Parameter		N ₂	Na ₂ SO ₃
No. of observations	n	5	5
Mean	\bar{x}	0.3193	0.3183
Sum of X	ΣX	1.5965	1.5916
Sum of X ²	ΣX^2	0.5104	0.5070
Variance	S ^{2a}	0.00015	0.00009
Standard deviation	S ^b	0.01225	0.00949
Coefficient of variation	CV ^c	3.83570	2.98046

$$^a S^2 = \Sigma_i (X - \bar{x})^2 / (n - 1).$$

$$^b S = \sqrt{S^2}.$$

$$^c CV = 100S / \bar{x}.$$

average of variance, the standard error, the mean, and the coefficient of variation of the experiment are shown in Table 3. To examine the significance of the difference between the treatments, t and f tests were performed on the data. The results are reported in Table 4.

DISCUSSION

The results of this study indicated that there were no significant differences between K_{La} values obtained from distilled-deionized water with different deoxygenation procedures. The results were very consistent and repeatable; the K_{La} mean was 0.3188 with a standard error of 0.0071 and coefficient of variation of 3.41%. Based on these results, it can be concluded that the unsteady state method with sulfite oxidation can be used effectively to evaluate aeration systems. The concentration of chemicals (15.8 mg/L sodium sulfite and 0.2 mg/L cobalt chloride) as suggested by Stukenberg et al. (8) are adequate and have no effect on K_{La}. Similar results were reported by Mills and Fenlon (3) and Ghaly (1) who used the unsteady state method with sulfite oxidation to evaluate the aeration capacity of oxidation ditch systems. In running their experiment, Mills and Fenlon (3) used the same water repeatedly with only one addition of 0.2 mg/L cobalt chloride. According to their results, the usage of the same water up to five times gave no significant discrepancies between replicates.

CONCLUSIONS

The use of sodium sulfite with cobalt chloride for deoxygenating the water is practical. The results are very consistent and repeatable. There was no effect of the chemical on DO measurements as performed with a DO probe.

Table 3
The Weighted Average of Variances, Standard Error, Mean, and Coefficient of Variability of the Experiment^a

Parameter		Value
Weighted average of variances	S_{12}^2	0.00013
Standard Error	Sd	0.00707
Mean	\bar{x}	0.31880
Coefficient of variation	CV	3.40808

$$^a \bar{x} = (\bar{x}_1 + \bar{x}_2)/2$$

$$\Sigma x_1^2 = \Sigma X_1^2 - (\Sigma X_1)^2/n \quad \text{where } n_1 = n_2 = n$$

$$\Sigma x_2^2 = \Sigma X_2^2 - (\Sigma X_2)^2/n$$

$$S_{12}^2 = \frac{\Sigma x_1^2 + \Sigma x_2^2}{2(n-1)}$$

$$Sd = \sqrt{\frac{2 S_{12}^2}{n}}$$

Table 4
Tests of Significance

t-test	f-test
t – tabulated at 0.05 = 2.306 at 0.01 = 3.355	f – tabulated at 0.05 = 5.32 at 0.01 = 11.26
t – calculated = $\frac{\bar{x}_1 - \bar{x}_2}{Sd}$ = $\frac{0.3193 - 0.3183}{0.00707}$ = 0.1414 NS	f – calculated = $\frac{S^2 \text{ from means}}{S^2 \text{ from individual}}$ = $\frac{0.00013}{0.00102}$ = 0.12745 NS

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