

# Effect of initial concentration of dissolved oxygen in aeration coefficient for long-term BOD experiments

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**ABSTRACT.** Long-term incubations of biochemical oxygen demand (BOD) were performed to determine the aeration coefficient derived from oxygen uptake experiments. The BOD bottles were prepared with distilled water and the incubation occurred in the dark, under controlled temperature (19.4°C). The bottles were submitted to two different treatments based on the initial dissolved oxygen (DO) concentrations (Treatment 1: 1.43mg L<sup>-1</sup> and Treatment 2: 7.67mg L<sup>-1</sup>). The DO concentrations were measured with an OD meter during 52 days. The results were fitted to a first-order kinetics model. The BOD bottles showed an increase in DO concentration for both treatments and the mean aeration coefficient ( $k_a$ ) was 0.065 a day<sup>-1</sup>. The fittings pointed to some dispersion in the  $k_a$  values, and the initial concentration of DO in the BOD bottles does not interfere in the aeration process, being a random process.

**Key words:** dissolved oxygen, aeration coefficient, long-term BOD experiment.

**RESUMO.** Efeito da concentração inicial de oxigênio no coeficiente de aeração para experimentos de DBO de longo prazo. Incubações de demanda bioquímica de oxigênio (DBO) de longo prazo foram realizadas para determinar o coeficiente de aeração proveniente de experimentos de consumo de oxigênio. Os frascos de DBO foram preparados com água destilada e incubados no escuro e sob temperatura controlada (19,4°C). Os frascos foram submetidos a dois tratamentos que foram baseados na concentração inicial de oxigênio dissolvido (OD: Tratamento 1 = 1,43mg L<sup>-1</sup> e Tratamento 2 = 7,67mg L<sup>-1</sup>). As concentrações de OD foram determinadas com oxímetro durante 52 dias. Os resultados foram ajustados a um modelo cinético de primeira ordem. Os frascos de DBO apresentaram um incremento nas concentrações de OD para ambos os tratamentos e o coeficiente de aeração ( $k_a$ ) foi de 0,065 dia<sup>-1</sup>. Os ajustes apontam dispersão nos valores de  $k_a$  e a concentração inicial de OD nos frascos de DBO não interferiu no processo de aeração sendo um processo aleatório.

**Palavras-chave:** oxigênio dissolvido, coeficiente de aeração, experimentos de DBO de longo prazo.

## Introduction

Biodegradation is an important mechanism in the organic matter removal in natural systems. Biochemical oxygen demand (BOD) is a widely used parameter for the determination of biodegradable organic compounds in aquatic systems, effluents and wastewater (Matos and Sousa, 1996; Hu *et al.*, 1999; Orupöld *et al.*, 1999). During aerobic degradation microorganisms oxidize organic matter in the presence of oxygen; as a result, dissolved oxygen (DO) is consumed by this oxidation. In 1925 Streeter and Phelps formulated a model that evaluated the BOD budget in aquatic

systems. Current water quality models are derived from the Streeter-Phelps model and include the effects of sedimentation, advection, dispersion, mixed-order model of BOD decay and aeration from the atmosphere (Rauch *et al.*, 1998; Tyagi *et al.*, 1999; Borsuk and Stow, 2000). The biological oxygen depletion was directly related with oxidation of the organic substrate by microbial communities under aerobic conditions (Henze *et al.*, 1997; Gotvajn and Zagorc-Koncan, 1999). The development of easy-to-use methods for practical applications is important for the mathematical modeling of ecological processes, which have

prompted researchers to perform experiments based on long-term BOD to assess the aerobic mineralization of organic substrates (Weijers, 1999; Brum *et al.*, 1999). The consumption of oxygen was related to the oxidation of an organic resource via first-order kinetics models (Characklis, 1990; Antonio *et al.*, 1999). The oxygen uptake curve reflects the aerobic mineralization kinetics of organic substrates.

According to Davis and Cornwell (1991) the depletion of DO and the effect of aeration can be described as:

$$\frac{dOC}{dt} = k_d L - k_a OC$$

where:

OC = the change in oxygen concentration per unit time [mg L<sup>-1</sup>],

L = total oxygen consumption [mg L<sup>-1</sup>] = ultimate OC,

k<sub>d</sub> = deoxygenation coefficient constant [day<sup>-1</sup>],

k<sub>a</sub> = aeration coefficient [day<sup>-1</sup>] derived from the method of DO determination by stirring the sample when using a probe to take DO measurements and,

t = time [day].

The experimental method used to assess the oxygen uptake from aerobic degradation assumes that aeration effects, due to handling and stirring procedures, occur during the experiment. Usually, the BOD test is free from this interference, because the samples are measured only once (e.g. at 5<sup>th</sup> day of incubation). The aeration process is intrinsic to the method of measuring dissolved oxygen concentrations in long-term aerobic mineralization experiments; with this respect, this study aims at determining k<sub>a</sub> and discussing the effect of DO initial concentration in the samples.

## Material and methods

To verify the aeration effect due to the stirring procedure during DO measurements in a long-term BOD experiment, assays were carried out in triplicates, in BOD bottles (1 liter) filled with sterile distilled water (autoclaved for 15 min, 1 atm and 121°C). The bottles were incubated in the dark and under different initial DO concentrations. The average incubation temperature was 19.40°C (SD = 0.16, n = 102; min: 18.7°C and max: 20.2°C). No microorganisms were added into the bottles as an inoculum. In order to reach low DO concentrations, the bottles from Treatment 1 (n=3) were boiled and then, bubbled with N<sub>2</sub> before

incubation. For Treatment 2, the bottles (n = 3) were oxygenated at room temperature, by bubbling clear filtered air during 1 hour, to keep DO near saturation concentrations. The mean initial DO concentration in Treatment 1 was 1.43 mg L<sup>-1</sup> (SD = 0.70, n = 3); for Treatment 2 this value was 7.67 mg L<sup>-1</sup> (SD = 0.04, n = 3).

The DO concentrations were measured periodically with an ODmeter (YSI - model 58) during 52 days (t = 0, 1, 2, 3, 6, 9, 10, 11, 12, 16, 20, 24, 28, 31, 35, 38, 43 and 52 days). Each measurement of DO concentration took approximately 20 s. The sampling days totaled 18 measurements; after each measurement, the bottles were closed and incubated in the dark. The progress of aeration was fitted to a first-order kinetics model, using a non-linear method (Levenberg-Marquardt iterative algorithm), according to Press *et al.* (1993). The t Test was applied to aeration coefficients, in order to check for significant differences (p ≤ 0.05) between the mean values of these coefficients.

## Results and discussion

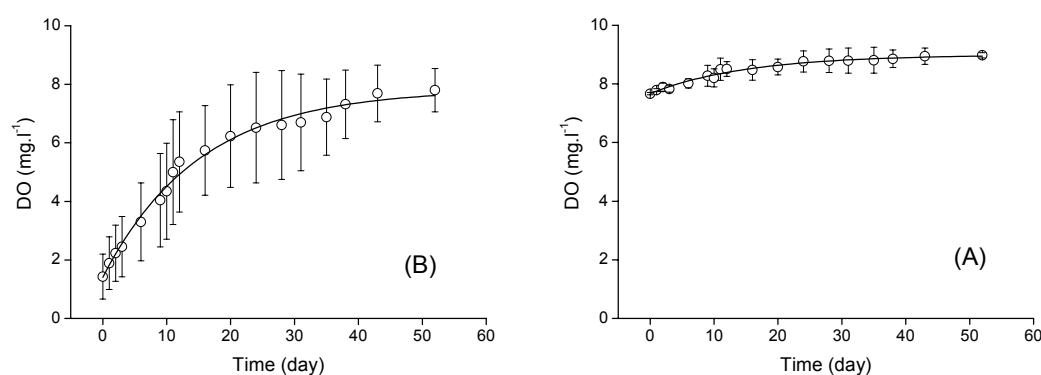
The progresses of aeration over time for Treatment 1 and 2 are illustrated in Figure 1. For all the bottles (1 to 6), a DO concentration increase was observed. Figure 1 includes the fittings of the cumulative oxygen enrichment, applying k<sub>d</sub> = 0 in the Equation of effect of aeration. Table 1 presents the parameterization of the kinetics fittings for the aeration processes. The fitting provides the aeration coefficient (k<sub>a</sub>) with a determination coefficient (r<sup>2</sup>) that ranged from 0.93 to 0.98. Table 1 also shows dispersion in k<sub>a</sub> values for both treatments. The initial DO concentration did not interfere on the determination of k<sub>a</sub>, which is a random process. The differences in k<sub>a</sub> for Treatments 1 and 2 can be attributed to the periodical handling of the samples, which could contaminate the media (distilled water). However, the caution in asepsis of the oxygen electrode was warranted. On the other hand, this kind of interference is inherent in long-term BOD experiments; they usually last an average of 45 days, and the samples are submitted to a large number of measurements (e.g. experiments performed by Farjalla *et al.*, 1999).

The differences in the incubation temperature and DO saturation percentages for each bottle interfered on the final OD concentration. The DO saturation percentages varied from 92.8 to 121%. These results indicate that the aeration process due to the long-term BOD experiment tended to increase the DO concentrations of the media even to saturation, independently of its initial DO

**Table 1.** Parameterization derived from the kinetics fitting of the aeration process from oxygen uptake experiments. Where:  $[DO]_i$  = initial concentration of DO;  $[DO]_f$  = final concentration of DO;  $DO_f$  = final concentration in relation to  $[OD]_{sat}$ ; T = incubation temperature;  $k_a$  = aeration coefficient;  $r^2$  = correlation coefficient and error derived from the fittings.

BOD bottle	$[DO]_i$ (mg L <sup>-1</sup> )	SD	$[DO]_f$ (mg L <sup>-1</sup> )	SD	$DO_f$ (%)	T (°C)	$k_a$	Error(*)	$r^2$
Treatment 1									
1	0.56	0.17	7.64	0.46	92.8	20.2	0.042	0.006	0.98
2	2.04	0.13	8.34	0.39	100	19.7	0.041	0.005	0.98
3	1.58	0.19	8.80	0.14	105	19.6	0.107	0.008	0.98
mean	1.40	0.13	7.82	0.17	-	-	0.066	0.005	0.98
Treatment 2									
4	7.68	0.05	10.15	1.37	121	19.2	0.013	0.009	0.93
5	7.71	0.05	8.90	0.06	105	18.7	0.068	0.011	0.96
6	7.64	0.09	9.23	0.07	109	18.8	0.095	0.016	0.94
mean	7.67	0.04	8.99	0.05	-	-	0.065	0.008	0.97
Treatments mean	-	-	-	-	-	-	0.0655	-	-

(\*) Error referred to the kinetics fittings



**Figure 1.** The cumulative oxygen aeration process in Treatment 1 (A) and Treatment 2 (B). The fittings using the kinetics model are shown as solid lines. The error bars indicate the standard deviation of the mean DO from bottles (D).

concentration. This process was slow as DO increases only a little during the course of the experiments. This interference can be treated as a residual error. Indeed, in some cases, the variation in DO ( $[DO]_{final} - [DO]_{initial}$ ) during the 52-day aeration process corresponded to only one day of variation, due to the deoxygenation in experiments with a high load of organic matter, as observed in oxygen uptake experiments with *Scirpus cubensis* ( $k_d = 0.00421 \text{ day}^{-1}$ ) and *Cabomba piauhyensis* ( $k_d = 0.00158 \text{ day}^{-1}$ ), in which 200 mg dry weight of these aquatic macrophytes tissues were used (Cunha and Bianchini Jr., 1998). Similar experiments with leaves, barks, branches and litter showed a mean  $k_d = 0.0031 \text{ day}^{-1}$  (Antonio *et al.*, 1999).

The fittings of the aeration processes with Treatments 1 and 2 led to very close mean values for  $k_a$  ( $0.0655 \text{ day}^{-1}$ ; t Test:  $t = 0.2815$ ). This value is similar to the aeration coefficient found for the oxygen uptake of low concentrations of tannic acid ( $k_a = 0.0651 \text{ day}^{-1}$ ); since oxygenation prevailed in

the mineralization of this polyphenol (Cunha-Santino and Bianchini Jr., 2003). Oxygen uptake experiments made by Bitar *et al.* (2002), with low concentrations of organic matter ( $20 \text{ mg L}^{-1}$ ), presented a mean  $k_d = 0.0463 \text{ day}^{-1}$  ( $n = 10$ ). The application of  $k_a$  obtained in this study to the experiments of oxygen uptake of aquatic macrophytes showed that the effect of aeration process in incubation with high concentrations of organic matter was attenuated or neutralized; this was probably due to the fact that the deoxygenation coefficient was more elevated, and the aeration effect was disguised. The latter are equally important under high concentrations of organic matter (Lemos and Bianchini Jr., 1998; Brum *et al.*, 1999). On the other hand, for incubations with low concentrations of organic matter (Cunha-Santino and Bianchini Jr., 2003) the effect of handling the samples can affect the budget between deoxygenation and aeration processes, resulting in an interference in the

determination of  $k_d$ , with the ultimate values for BOD being underestimated.

### Conclusion

According to the methodological procedures adopted, the results demonstrate that the initial concentration of DO from the samples used in long-term BOD experiments does not interfere in the aeration process, being a random process. For all initial DO concentrations, the aeration coefficient ( $k_a$ ) did not depend on the oxid condition of the sample. In relation to the application of these results, we suggest the use of  $k_a$  when modeling oxygen uptake experiments with low load of organic matter, but not in experiments with high loads of organic matter, where the effect of aeration is neutralized or attenuated by oxidation.

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