Research Journal of Agriculture and Biological Sciences, 2(3): 109-114, 2006

A Detailed Statistical Assessment of Methods for Nitrification Parameters

[1]I.A. Oke, [2]J.A. Otun, [3]N.O. Olarinoye and [2]I. Abubakar

[1]Department of Civil Engineering, Obafemi Awolowo University, IleIfe, Nigeria
[2]Department of Chemistry, Adeyemi College of Education, Ondo, Nigeria
[3]Department of Water Resources and Environmental Engineering, Ahmadu Bello University, Zaria,

Abstract: With increasing more and more restrictive effluent quality by water authorities, conventional treatment such as biological treatment discharges with less than 99% nitrogenous compounds removal may no longer be tolerated. Well-designed nitrification processes hold a great promise to provide better treatment and protection of environment in term of nitrogenous compounds removal. In the design of nitrification facilities accurate nitrification parameters are essential. The methods for the determinations of the parameters are many, among which are linear logarithmic, power function, fibonacci and non-liner regression methods. In this paper, a report on a the statistical assessment of these methods using statistical methods (total error, CD and MSC) was presented with a particular attention been paid to the accuracy, validity and goodness of fit of each the methods. The study shows that averages of total error are 95.58, 38.64, 249.82 and 39.92, averages of CD are 0.964,0.995, 0.789 and 0.994 and averages of MSC are 2.69, 2.64, 1.06 and 2.56 for linear logarithmic, non-linear regression, Fibonacci and power function methods respectively. The accuracy, validity and goodness of fit of these methods are in order of non-linear regression (0.995) > power function (0.994) >linear logarithmic (0.964) > Fibonacci (0.789) on basis of averages of CD. In selection for practical uses: power function (39.92) > non linear regression (38.64) > linear logarithmic (95.58) > Fibonacci (249.82) on the basis of averages of MSC and applicability.

Keywords: Wastewater, biological treatment process, methods of determining nitrification rate, total error, model of selection criterion, coefficient of determination.

INTRODUCTION

Industrial wastewaters contain high levels of various toxic compounds (such as nitrogenous compounds) that interfere with aquatic and terrestrial life when released into land and water ecosystems. Nitrogen exists in four forms in the aquatic environment, namely: organic nitrogen, nitrate, nitrite and ammonia[1]. All nitrogenous compounds are of interest, especially nitrate, which is a strong metal ligand. This also makes it difficult to remove trace metal pollutants still contained within the wastewater. Most of the nitrogen in treated wastewater is in the form of ammonia. Consequently, when wastewater-containing ammonia is discharged into the environment, depletion of receiving water body oxygen resources can occur as the ammonia is oxidised to nitrate. This depletion of oxygen can be eliminated if the ammonia is first oxidised to nitrate before it is discharged into the environment. It is well known that the ratio of ammonia concentration (toxic form) to ammonium ions (relatively non-toxic) increases with rising temperature and pH. Tannery mill's effluents usually contain high amounts of ammonia and/or nitrate ions owing to the use of hides and skins[2]. Various non-biological methods are available for the removal of these compounds from wastewaters but they are expensive and the disposal of the end product becomes problematic (for example using reverse osmosis the end product is a concentrated waste brine which becomes difficult to dispose of). Biological methods are easier to operate and maintain and are consequently cheaper. Often the end products are harmless and their disposal is easier. Biological removal of ammonia and nitrate from municipal and industrial wastewaters are a well established practice with a number of widely used process designs, from the earliest oxidation ditches to the more recent discoveries of the Anammox[3], Canon[4] and Sharon[5] processes. Apart from Anammox, biological removal of ammonia (nitrification) is traditionally defined as the aerobic oxidation of ammonia to nitrate through nitrite. This is mainly carried out by two groups of autotrophic bacteria; ammonia oxidisers, exemplified by Nitrosococcus and Nitrosomonas spp., and nitrite oxidisers such as Nitrobacter and Nitrospira spp (Nitrification process takes place in two stages by

Corresponding Author: I.A. Oke, Department of Civil Engineering, Obafemi Awolowo University, IleIfe, Nigeria
E-mail: okeia@oauife.edu.ng

nitrifying autotrophic bacteria as summarised by the following reactions as shown in equations (1), (2) and (3). It can be accomplished in any of the suspended growth systems such as activated sludge processes and lagoons. It can also be accomplished in attached growth processes, namely: the trickling filter and the rotating biological contactor. The advantages of the various nitrification processes are well documented[1,6,7].

$$NH_4^+ + 1.5O_2 \xrightarrow{\text{Nitrosomonas}} NO_2 + 2H^+ + H_2O \quad (1)$$

$$NO_2^- + 0.5O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- \quad (2)$$

overall equation of the reaction is

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O \quad (3)$$

A well-designed nitrification process can reduce nitrate concentration from 94 mg/L to less than 30 mg/L, 57 mg/L to less than 20 mg/L and 10 mg/L to nothing in 1000hours[8], 16.96 – 101 mg/L to 1.92 – 7.80 mg/l of nitrate as nitrogen in 80 days[9]. Nitrification will occur in most aerobic biological treatment processes when the operating and environmental conditions are suitable. In activated sludge process one of the important controlling variables is the mean cell residence time. Dan *et al*.,[10], Vredenbregt et al.,[11] provide data on nitrification under extreme conditions. Oxidation of nitrogenous compounds in wastewater may be conveniently monitored on the basis of the following mass balance equation (4):

$$S_{N0} = S_{N0O} + \frac{\mu_A X_{AO}}{Y_A(\mu_A - b_A)} e^{(\mu_A - b_A)t} - \frac{\mu_A X_{AO}}{Y_A(\mu_A - b_A)} \quad (4)$$

In nitrification kinetic (equation 4) the essential parameters are k, X_{AO}, Y_A and m_A. They are usually use in the design facility for nitrification process. The methods for solving nitrification kinetic are numerous, namely: linear logarithmic, power and fibonacci technique[2] and non-linear regression.

In linear logarithmic method equation (4) is often simplified into a simpler linear logarithmic form for the calculation of the corresponding $\mu_A - b_A$ value. In power function Orhon *et al.*,[2] proposed a “curve fitting” approach for the solution. Equation (4) was transformed into equations (5) and (6) for monitoring nitrification process:

$$(S_{N0} - S_{N0O})k + 1 = e^{at} \quad (5)$$

$$k = \frac{Y_A}{X_{AO}} \frac{\mu_A - b_A}{\mu_A} \quad \text{and} \quad a = \mu_A - b_A \quad (6)$$

Documentation on accuracy, valid and the goodness of fit of each of these methods are rare. Therefore there is a need for statistical evaluation of these three methods considering the important of the parameters in the design for nitrification process. The main objective of this study is to evaluate the methods statistically with a particular attention to accuracy, validity and goodness of fit using total error, coefficient of determination (CD), model of selection criterion (MSC) and non-parametric tests.

MATERIALS AND METHODS

Wastewater samples were collected from an influent into institutional waste stabilization ponds (Obafemi Awolowo University, Ile-Ife, Nigeria). The samples were collected weekly for five months and seeded with mix liquor suspended solids from the pond as stated in APHA[12]. The BOD removed were determined on the samples continuously for 20 days according to Standard Methods as specified in APHA[12] using BOD meter method (CAMLAB HACH, model number 2173B BOD manufactured by Hach Chemical Company). The weekly average for each month were used for computations. The first 10 days BOD were for carbonaceous oxygen demand and the last 10 days for nitrogenous oxygen demand (nitrification). Calculations of the parameters (k and μ_A - b_A) were carried out using the four methods (power function, fibonacci, linear logarithmic and non-linear regression methods). Computations of BOD were carried out using expression:

$$BOD_t = \frac{(D_1 - D_2) - (B_1 - B_2)f}{p} \quad (1)$$

RESULTS AND DISCUSSION

The results of the nitrification analysis using these methods are shown in Table 1. The μ_A - b_A ranges from 0.022 to 0.646 /d. These values were similar to the μ_A - b_A documented in literature such as Adewumi *et al*.,[13], (2005) for the institutional wastewater and Metcalf and Eddy[1] for strong domestic wastewaters. A statistical analysis (ANOVA) of the μ_A - b_A indicates that there is a significant difference between the μ_A - b_A at 99 percent confidence level. Also, it was found that there is a significant difference between the methods at 99 percent confidence level. This indicates that μ_A - b_A is a function of method used. It indicates that the values of μ_A - b_A vary with the method of determinations used and period. Like μ_A - b_A Table 1 shows the values of K. The minimum value is 7.42 and 1143.04 as the maximum. The ANOVA of the K establishes that there is a significant difference between the methods used at 99 % confidence level.

Statistical values (total error, coefficient of determination and model selection criterion) were determined from each of these data to ascertain the goodness of fit, accuracy and validity of the data. The

Table 1: The values of ultimate BOD and rate of reaction.

Methods	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Mean	Standard deviation
	μ_A - b_A (/d)						
Linear-logarithmic	0.395	0.255	0.437	0.337	0.359	0.357	0.061
Non- Linear	0.033	0.074	0.071	0.052	0.022	0.05	0.02
Fibonacci	0.254	0.393	0.277	0.244	0.31	0.296	0.054
Power function	0.414	0.646	0.519	0.366	0.38	0.465	0.105
	K						
Linear-logarithmic	39.03	37.43	34.68	49.04	31.64	38.36	5.9
Non- Linear	741.83	208.54	220.54	589.02	1143.04	580.59	347.42
Fibonacci	20.27	7.42	12.87	25.69	8.38	14.93	7.04
Power function	28.36	7.67	13.32	48.17	33.48	26.2	14.49

Table 2: Total error, CD and MSC of the methods using ultimate BOD

Methods	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Mean	Standard deviation
	Total error						
Linear-logarithmic	99	82.3	80.7	135.5	80.4	95.58	21.14
Non- Linear	44	38.2	26.3	53.9	30.8	38.64	9.75
Fibonacci	228.1	189.2	160.1	360.7	311	249.82	75.14
Power function	44.9	43	25.9	40.6	45.2	39.92	7.2
	Coefficient of determination (CD)						
Linear-logarithmic	0.965	0.957	0.96	0.961	0.976	0.964	0.007
Non- Linear	0.994	0.992	0.996	0.995	0.997	0.995	0.002
Fibonacci	0.836	0.8	0.86	0.777	0.671	0.784	0.065
Power function	0.994	0.99	0.996	0.997	0.993	0.944	0.002
	Model of Selection criterion (MSC)						
Linear-logarithmic	2.7	2.49	2.56	2.66	3.05	2.69	0.194
Non- Linear	2.43	2.22	2.93	2.58	3.05	2.64	0.309
Fibonacci	0.86	0.97	0.68	1.22	1.58	1.06	0.313
Power function	2.4	1.99	2.97	3.14	2.28	2.56	0.432

total error, which is the sum of the squares of the errors between the obtained values and the predicted values can be interpreted as a measure of variation in the values predicted unexplained by the values obtained data. The lower the value of total error the higher the accuracy, validity and goodness of fit of the method[14]. Total error (Err^2) can be computed using equation (4):

$$Err^2 = \sum_{i=1}^{2} \left(Y_{obsi} - Y_{cali}\right)^2 \quad (4)$$

The coefficient of determination (CD) can be interpreted as the proportion of expected data variation that can be explained by the obtained data. Higher values of CD indicate higher accuracy, validity and goodness of fit of the method. CD can be expressed as follows[15]:

$$CD = \frac{\sum_{i=1}^{2} \left(Y_{obsi} - \overline{Y_{cali}}\right)^2 - \sum_{i=1}^{n} \left(Y_{obsi} - Y_{cali}\right)^2}{\sum_{i=1}^{n} \left(Y_{obsi} - \overline{Y_{cali}}\right)^2} \quad (5)$$

The model selection criterion (MSC) is interpreted as the proportion of expected data variation that can be explained by the obtained data. Like, CD the higher the value of MSC, the higher the accuracy, validity and the

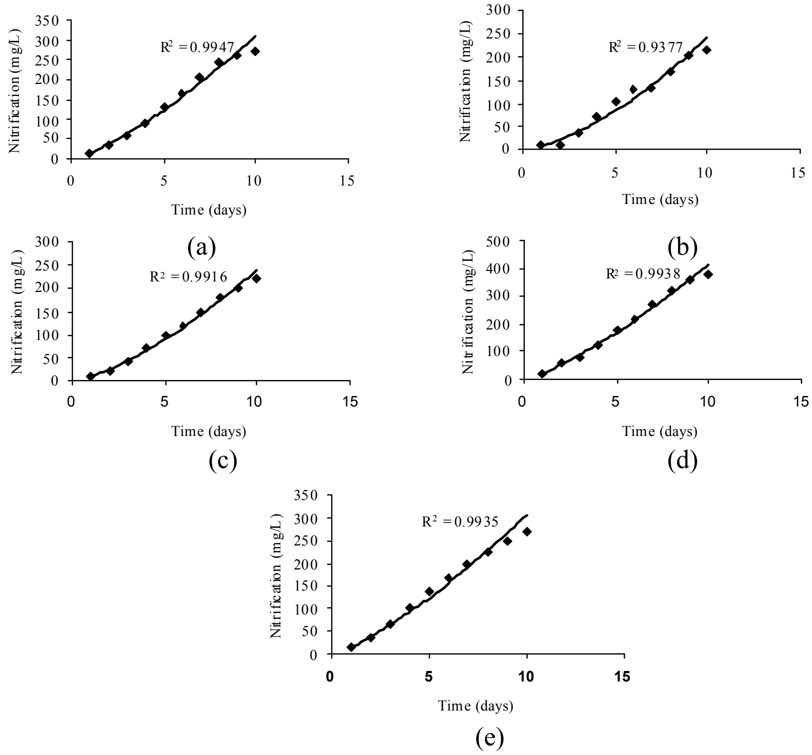

Fig. 1: Non-linear plots of the experimental data (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4 and (e) sample 5

goodness of fit of the method. MSC can be computed using equation (6) as follows:

$$MSC = \ln \frac{\sum_{i=1}^{2}\left(Y_{obsi} - \overline{Y_{obs}}\right)^2}{\sum_{i=1}^{2}\left(Y_{obsi} - Y_{cali}\right)^2} - \frac{2p}{n} \qquad (6)$$

The results of statistical evaluation are shown in Table 2. It is clear that using a non-linear regression and power function methods resulted (in all cases) in the smallest error, the highest CD and the highest MSC. The values of statistical evaluation (total error, CD and MSC) indicate that non-linear regression or power function should be the first choice when considering analysis of nitrification results for μ_A - b_A and K determination. Figures 1a, b, c, d and e show the experimental data for all samples together with the fitting that resulted when plotting the power function method. This result is similar to observation made on non-linear regression (that is it is the best approach for polynomial equations such as BOD removal[14,15]. The linear logarithmic method has the next ranks. Although, the method can be easily implemented in an electronic spreadsheet, Microsoft excels and most plotting packages have it built in too. The drawback is that it gives larger errors than non-linear regression and power function methods, lower CD and MSC due to the discrete of fitting a curve into a linear equation at each of the data points. The Fibonacci technique (which is next in term of validity and accuracy is also easy to implement) originated from the similarity in shapes of an arbitrary mathematical function with that of the nitrification or BOD curve. The results of total error, CD and MSC show that the mathematical function is always true for nitrification curves. Although, the method can be easily implemented manually, its drawback is that it gives larger errors due to the discrete estimation of the slope.

Non parametric tests of the two approaches: The results from the four methods were subjected to non parametric test (Friedman, Kendall and Wilcoxon tests) as described in Guttman *et al.*,[16] and Loveday[17]. The results of non parametric test are as shown in Table 3. Results of Friendman test indicates that there is no significant difference between the experimental data and the data obtained from Non-linear regression, linear logarithms and power function methods, but there is a significant difference between results from fibonacci method. Results of Kendall and Wilcoxon tests indicate that Fibonacci technique in not applicable in estimating parameters for nitrification kinetic, while power function agreed perfectly with experimental data.

Table 3: Results of non-parametric tests

		Wilcoxon Test			Kendall test
Methods	Friedman	Positive	Negative	Significant	Kendall's coefficient of concordance
Non- Linear	0.72	25.64	25.39	0.475	0.014
Fibonacci	42.32	25.17	33.5	0	0.846
Power function	0	28.16	22.84	0.521	0
Linear-logarithmic	0.72	28.55	23.11	0.927	0.014

Conclusion: It can be concluded based on the result of the study that: linear-logarithms, non-linear regression and power function methods should be used as an alternative to other methods for nitrification kinetic parameters determination the method is statistically and mathematically valuable and justifiable.

Abbreviation, symbols and acronyms:

D_1 and D_2 initial and final dissolved oxygen of the sample respectively (mg/L) ratio of seed in the sample to seed in the controlp decimal volumetric fraction of sample used.

B_1 and B_2 initial and final dissolved oxygen of the seeded control respectively (mg/L) m_A maximum growth rate for autotrophic biomass, /d

b_A specific decay rate of autotrophic biomass, /d

S_{NO} oxidised N concentration, mg··/L

S_{NO0} initial concentration of oxidised N, mg·/L

t time, d

Y_A overall yield coefficient of autotrophic biomass, g cell COD(g oxidised N)1

X_{A0} initial concentration of autotrophic biomass, mg·/L

CD coefficient of determination

Err^2 total error

MSC model selection criterionn number of data points

p number of parameters

Y_{cali} expected values of each fitting procedure

Y_{obs} average of obtained (experimental) values

Y_{obsi} obtained (experimental) values

REFERENCES

1. Metcalf and Eddy Inc., 1991. Wastewater Engineering Treatment Disposal and Reuse, 3rd edn, McGraw-Hill Book Company, New York.
2. Orhon, D., E. Ates and S. Sözen 2000. Experimental evaluation of the nitrification kinetics for tannery wastewaters', Water SA., 26: 43-52
3. Mulder, A., A. Van De Graaf, L.A. Robertson and J.G. Kuenen, 1995. Anaerobic ammonium oxidation discovered in a denitri-fying. uidized bed reactor. FEMS Microbiol. Ecol. 16: 177-183.
4. Schmid, T.I., O. Sliekers, M. Schmid, E. Bock, J. Fuerst, J.G. Kuenen, M.S.M. Jetten and M. Strous, 2003. New concepts of microbial treatment processes for the nitrogen removal in waste water. FEMS Microbiol. Rev., 27: 481-492.
5. Hellinga, C., A.A. Schellen, J.W. Mulder, M.C.M. Van Loos-Drecht and J.J. Heijnen, 1998. The Sharon process: an innovative method for nitrogen removal from ammonium-rich waste water. Water Sci. Technol., 37: 135-142.
6. Horan, N.J., 1993. Biological Wastewater Treatment System, Theory and Operation, 1st Edn., John Wiley and Sons, New York
7. Noyes, R., 1994. Unit Operations in Environmental Engineering, 1st Edn., Noyes Publication, New Jersey.
8. Darbi, A., T. Vuraraghavan, R. Butler and D. Corkal, 2002. Batch studies on Nitrate removal from potable water. Water SA., 28: 319-322.
9. Kasla, J.M., J.R. Duncan, and J.E. Burgess, 2005. Biological Removal of Nitrogen Species from Metal Processing Wastewater, Water SA., 31: 407-412.
10. Dan, N.P., C. Visvanathan and B. Basu, 2003. Comparative evaluation of yeast and bacterial treatment of high salinity wastewater based on biokinetic coefficients. Bioresour. Technol., 87: 51-56.
11. Vredenbregt, L.H.J., K. Nielsen, A.A. Potma, G.H. Kristensen and C. Sund, 1997. Fluid bed biological nitrification and denitrification in high salinity wastewater. Water Sci. Technol., 36: 93-100.
12. APHA, 1998. Standard Method for the Examination of Water and Wastewater, 20th Edn., America Water Works Association and Water Pollution Control Federation, Washington DC.
13. Adewumi, I.K., I.A. Oke and P.A. Bamgboye. 2005. Determination of the Deoxygenation rates of a residential Institution's Wastewater. J. Appl. Sci., 5: 108-112.
14. Oke, I.A. and A.A. Akindahunsi, 2005. A Statistical Evaluation of Methods of Determining BOD rate. J. Appl. Sci. Res., 1: 223-227.

15. Gullemo, C., M. Liliana, E.V. Carlos and J.F. Gonzales, 1999. A short note on the determination of the kinetics parameters for the BOD test. Water SA., 25: 377-380.
16. Guttman, I., S.S. Wilks and J.S. Hunter, 1971. Introductory Engineering Statistics, 2nd Edn., John Wiley and Sons Inc, New York.
17. Loveday, R., 1980. Statistics, A second course in statistics, 2nd Edn, University Press Cambridge.