BOD_5 REMOVAL KINETICS OF STABILIZATION POND SYSTEMS IN NORTH GREECE

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ABSTRACT

Wastewater stabilization ponds (WSPs) are one of the simplest techniques available for the treatment of municipal Wastewater. Although many WSPs have been established and made in operation in several countries, in Greece the use of them is limited. As well as, the dynamics of pollutants in these systems are not well known. The aim of the present work is the determination of BOD_5 removal kinetics of full –scale WSPs systems situated in the North part of Greece, treated municipal wastewater, as the removal of organic matter (BOD_5) is one of the primary goal of systems design. The study estimates this design parameter pertaining to local conditions to optimize the design considerations and sizing requirements using first order, Monod type, Konė Type and Kadlec and Knight type models. The estimated parameters can effectively be applied in sizing WSP in Mediterranean climatic conditions.

Three WSP systems are examined. They are situated in a lowland area in mainland of northern Greece in latitude φ: 41° up to 41°15', longitude λ: 23°21΄ up to 23°36΄ and altitude from 14m to 52. They consist of one facultative pond, one (N. Skopos) or two (Vamvakofito, Charopo) maturation ponds and a rock filter before the final discharge for algae filtration. Every system has a different total hydraulic retention time (HRT). The systems were monitored for approximately three years. For each system instantaneous samples were taken from the inflow of the 1st pond and the outflow of the last pond, during the years 2006, 2007 and 2012, twice a month, while meteorological data were recorded. The outflow data have corrected by mass balance method to eliminate errors from atmospheric precipitation, rainfall and evapotranspiration.

The models were evaluated by comparing the real observed values F (Cin, Cout) of stabilization ponds collected data with the predicted by the equations values. To evaluate model performance, efficiency criteria are defined as mathematical measures of how well the model simulation fits the available observations. The used efficiency criteria, was the coefficient of determination r^2, the Nash-Sutclife efficiency E and the unitized risk or coefficient of variation CV.

The Kickuth Equation which used typically in the design of stabilization ponds, showed a good mathematical relationship between theoretical predicted results and site data. Using this simple equation for all the collected data from the three WSP systems, after calibration, it can be proposed the value 0.091 [d^{-1}] for the BOD_5 biodegradation rate constant (K). The rate constant (K) has a very strong relationship with HRT (R^2 = 0.9999**)** expressed as K = 0.3579 – 0.004d, where d is the HRT in days. As well as, for the (K) the value 3.67 $g\ BOD_5\ m^{-2}d^{-1}$ can suggest.

Keywords: wastewater, stabilization ponds, BOD_5 removal rate, kinetic, biodegradation rate constant.

1. Introduction

Wastewater Stabilization Ponds (WSPs) are a simple in engineering terms construction, but they are extremely complex as ecological systems (S. Kayombo *et al*, 2005). Most empirical model or design tools developed and used on-site or regionally-specific WSPs data. Different characte-ristics, in terms of climate and hydrology, can lead to problems when models are transferred without appropriate modification for local conditions. For example the removal of pathogenic organisms has a high priority in tropical climate, whereas nutrient removal in European regions has a high priority (S. Kayombo *et al*, 2005). Thus, as WSPs are a sensitive ecological system, not all models can be transferred and used in all countries. Using a “uniform:” simple methods, often the results are malfunctions or a reduced efficiency of WSP’s system (Tilley E., 2014). Although many of the WSP design tools and models have been adopted from countries with temperate climates there are not many information about the dynamics of pollutants in these systems. Lack of such information was the impetus for this work. The aim of the present work is the determination of BOD_5 removal kinetics of three full –scale WSPs systems situated in the North part of Greece, treated municipal wastewater, as the removal of organic matter (BOD_5) is one of the primary goal of systems design. The study estimates the biodegradation rate constant (K) pertaining to local conditions to optimize the design considerations and sizing requirements using several kinetic models. The estimated parameters can effectively be applied in sizing WSP in Mediterranean climatic conditions.

2. Materials and methods

2.1. Data

All the three systems are situated in a lowland area in mainland of northern Greece in latitude φ: 41° up to 41°15’, longitude λ: 23°21´ up to 23°36´ and altitude from 14m to 52. They treat only domestic wastewater and consist of one facultative pond, one (N. Skopos) or two (Vamvakofito, Charopo) maturation ponds and a rock filter before the final discharge for algae filtration. Every system has a different total hydraulic retention time (HRT). Skopos’ HRT is 18.6 d for Vamvakofito is 68.7 d and for Charopo 72.4 d. The systems were monitored for approximately three years. For each system instantaneous samples were taken from the inflow of the 1st pond and the outflow of the last pond, during the years 2006, 2007 and 2012, twice a month, at least (Chalatsi M, 2014). The samples were collected approximately at the same morning period, while meteorological data were recorded. The samples were placed into 1000 ml polyethylene bottles, and were transferred immediately to the wastewater laboratory of Serres City (Chalatsi M, 2014). To enhance the range and accuracy of data, each of samples was analyzed separately twice and the averages were considered. The outflow data have corrected by mass balance method to eliminate errors from atmospheric precipitation, rainfall and evapotranspiration. The H_{rain} obtained by Hellenic Meteo Service, Bureau of Serres and the evapotranspiration has calculated using Thornthwaite method (1948) (Kuo J.,2014), as many researchers believe that the mass balance is the most authoritative method to approach mechanisms and parameters that determine the performance of natural systems and the changes occurring in these (Breen 1990, Heliotis and DeWitt 1983, Howard-Williams 1985, Korkusuz 2004).

2.2. Kinetic Models

There are several kinetic models in the literature, used to evaluate the biodegradation rate constant (K). The most common models described stabilization pond kinetic are the combined model of first-order and Plug flow, the combined model of first order and CSTR (Continuous flow Stirred Tank Reactors) regime, the combined model of Plug flow and Monod, and the combined model of Monod and CSTR (Gil Penha-Lopes *et al* 2012, Rasoul Khusravi *et al* 2013, Chlot *et al* 2011). All equations derived from the mentioned combinations can be expressed as the general formula:

$$K = f(C_{in}, C_{out})\,\frac{Q}{A}$$

Where K is the first-order kinetic constant for organic pollutant removal, Q is the flow rate [m^3/d], A is the pond area [m^2] C_{in} is the input pollutant concentration [mg/L] C_{out} is the output pollutant concentration [mg/L].

Combining of first-order reaction kinetic and Plug flow regime creates the first design equation (Equation Kickuth) which is the most widely used equation in WSPs and wetlands design.

$$K_1 = \frac{Q}{A}\ln(C_{in}-C_{out}) \quad , \quad [m\ d^{-1}] \qquad (1)$$

The combined model of first order and CSTR gives the following simple equation:

$$K_2 = \frac{Q(C_{in}-C_{out})}{A(C_{out})} \quad , \quad [m\ d^{-1}] \qquad (2)$$

From the combination of Plug flow model and Monod equation $\frac{dc}{dt}=-K_{max}\frac{C}{C+C_{half}}$, the following equation (Eq. 3) is derived under the consideration that K_{max} has been equal to 60 mg/L, that is the common value used in Monod's Equation (Rasoul Khusravi *et al* 2013) in WSPs.

$$K_3 = \frac{Q}{A}[(C_{in}-C_{out})+60\ln(\frac{C_{in}}{C_{out}})] \quad , \quad [g\ BOD_5\ m^{-2}d^{-1}] \qquad (3)$$

Where K_{max} is the maximum BOD_5 removed in WSPs regardless the effect of temperature [$g/m^3.d$], C_{half} is the amount of wastewater BOD_5 while the removed BOD_5 value is half of K_{max}. While, the combined model of Monod equation and CSTR gives the equation 4 for the estimation of first-order kinetic constant k_4, under the same consideration concerning the K_{max}.

$$K_4 = \frac{Q}{A}\frac{(C_{in}-C_{out})(60+C_{out})}{C_{out}} \quad , \quad [g\ BOD_5\ m^{-2}d^{-1}] \qquad (4)$$

These models describe the kinetic, without considering the consumption of substrate. Zwietering *et al,* (1990) derived a modified mathematical relationship based on the Gompertz model for the increase in biomass over time, which relates the population size over time to the specific growth rate, lag time, and asymptotic level of organisms. Kadlec and Knight (1996) developed a model, for wetlands, that is a combination of the basic equation of the plug flow model and the aqueous mass balance. This model is known as K-C* model. It differs from the original Kickuth equation in two ways. It is a reversible first-order reaction equation and includes a non-zero substrate concentration. It describes better the removal of pollutants, as they cannot be reduced to zero in wetlands or in the ponds, due to the subsequent release of pollutants from the ponds into the treated water. The non-zero background concentration represents in more realistic way the pollutants resulting from transformation processes within the sediments and from the interactions between the sediments and the wastewater. The main reason of these processes is the production of organics from the decomposition of organic materials and the endogenous autotrophic processes (IWA 2000, Ronnie A. D. Frazer-Williams 2010). The substrate utilization rate was directly related to the specific growth rate of heterotrophic bacteria in the stabilization ponds, as also was shown by N. Panikov in 2000 and S. Kayombo *et al* in 2003. As the examined stabilization pond systems have characteristics similar with wetlands this model can be used. The K-C* model is written as in the equation 5.

$$K_5=\frac{Q}{A}\ln\left(\frac{C_{in}-C^*}{C_{out}-C^*}\right) \quad , \quad [m\ d^{-1}] \qquad (5)$$

Where k_5 is the first-order kinetic constant and C* is non-zero background [mg/L]. The value of C*, according Kadlec and Knight (1996), for pollutant parameters used in this study, is equal to $3.5 + 0.053\ C_{in.}$

All the above mentioned equations are used in this study. The models assessment, the accuracy and reliability of the results are evaluated by comparison with existing real data. As the equations are closer to the mathematical calculation, as more accurate models they would be. For each stabilization pond system, the value of "K_{BOD}" is being obtained both as calibration from linear regression and as the median of predicted values.

2.3. Statistic Analysis

The models denominated by Equations 1 to 5 were evaluated by comparing the real observed values F (Cin, Cout) of stabilization ponds collected data with the predicted by the equations values. To evaluate model performance, efficiency criteria are defined as mathematical measures of how well the model simulation fits the available observations (P. Krause *et al*, 2005). The used efficiency criteria, in this study, was (i) the coefficient of determination r^2, defined as the squared value of the coefficient of correlation according to Bravais-Pearson. The range of r^2 lies between

0 (no correlation) and 1.0 (the dispersion of the prediction is equal to that of observation). The fact that only the dispersion is quantified is one of the major drawbacks of r^2 if it is considered alone is advisable to take into account additional information which can cope with that problem. (ii) The Nash-Sutclife efficiency E. The range of E lies between 1.0 (perfect fit) and - ∞. An efficiency of lower than zero indicates that the mean value of the observed time series would have been a better predictor than the model. (iii) The unitized risk or coefficient of variation CV that is defined as the ratio of the standard deviation σ to the mean μ. It shows the extent of variability in relation to the mean of the population. CV measures are often used as quality controls for quantitative laboratory assays. As closer to zero is CV value so better the fit. The combination of the above criteria gives more information about the efficiency of used equations.

3. Results and discusion

The obtained values of "K_{BOD}", after the mathematical and statistical processing of the collected data are presented as following in tables 1,2,3.

Table 1: Stabilization Ponds of Charopo – BOD_5 biodegradation rate constant (K)

Equation	1	2	3	4	5
	md^{-1}	*md^{-1}*	*$g\ BOD_5\ m^{-2}d^{-1}$*	*$g\ BOD_5\ m^{-2}d^{-1}$*	*md^{-1}*
K_{BOD}	0.065303	0.014184	1.312474	1.512003	0.012090
r^2	0.866216	0.866217	0.899758	0.874033	0.866217
E	0.860286	0.857351	0.893614	0.886338	0.768457
CV	0.056434	0.270267	0.147316	0.184373	0.234008
R^2 (K_i vs % removal)	0.986000	0.973100	0.752800	0.906700	0.976600
Median	0.064720	0.016530	1.326560	1.597190	0.013695
STD	0.003673	0.004294	0.193348	0.292545	0.003098
MIN	0.055690	0.006546	0.822847	0.882650	0.006231
MAX	0.071789	0.023221	1.623317	2.006131	0.018674

Table 2: Stabilization Ponds of Vamvakofito – BOD_5 biodegradation rate constant (K)

Equation	1	2	3	4	5
	d^{-1}	*md^{-1}*	*$g\ BOD_5\ m^{-2}d^{-1}$*	*$g\ BOD_5\ m^{-2}d^{-1}$*	*md^{-1}*
K_{BOD}	0.082510	0.027763	2.922987	3.668164	0.019799
r^2	0.779028	0.773289	0.771706	0.685787	0.773289
E	0.959798	0.859390	0,407023	0.795733	0.771296
CV	0.044692	0.182621	0.145760	0.154181	0.131276
R^2 (K_i vs % removal)	0.985300	0.987100	0.351800	0.621000	0.989000
Median	0.090723	0.027198	2.916601	3.566146	0.019482
STD	0.004056	0.005176	0.426054	0.550280	0.002632
MIN	0.080730	0.018759	1.957796	2.336043	0.014915
MAX	0.097913	0.038225	3.824957	4.762412	0.025224

Taking into account all the equations efficiency criteria for the WSPs system of Charopo the equations 1 and 3 give better results. For this system as K_{BOD} value, suggested rates 0.065303 [md^{-1}] or 1.312474 [$g\ BOD_5\ m^{-2}d^{-1}$]. It is obviously that the equations 1 give better results for both WSP systems Vamvakofito and Skopos. The suggested K_{BOD} value is 0.082510 [md^{-1}] and 0.282898 [md^{-1}], respectively. To choose between equations 3 and 4 it was taking into account additional the R^2 of Regression for the effect of K coefficient on BOD mass removal, for the WSP systems of Vamvakofito and Skopos. The equation 4 gives better results. For Vamvakofito system, as K_{BOD} value, suggested rate is 3.668164 [$g\ BOD_5\ m^{-2}d^{-1}$] and for Skopos one the values is 9.03715 [$g\ BOD_5\ m^{-2}d^{-1}$].

Table 3: Stabilization Ponds of N.Skopos – BOD_5 biodegradation rate constant (K)

Equation	1	2	3	4	5
	md^{-1}	*md^{-1}*	*$g\ BOD_5\ m^{-2}d^{-1}$*	*$g\ BOD_5\ m^{-2}d^{-1}$*	*md^{-1}*
K_{BOD}	0.282898	0.069118	6.636281	9.03715	0.054870
r^2	0.971157	0.971157	0.968884	0.970162	0.971157
E	0.969642	0.204140	0.799436	0.913421	0.966248
CV	0.095260	0.150785	0.145760	0.203312	0.121550
R^2 (K_i vs % removal)	0.965100	0.995600	0.046600	0.160900	0.965100
Median	0.269076	0.070615	7.405328	10.43636	0.057919
STD	0.026422	0.010793	1.524532	0.026422	0.006953
MIN	0.237783	0.053544	7.005506	5.777556	0.045788
MAX	0.339523	0.092082	13.68670	11.16875	0.068992

The Equation Kickuth (Eq. 1) which used typically in the design of stabilization ponds, showed a good mathematical relationship between theoretical predicted results and site data. Using this simple equation for all the collected data from the three WSP systems, after calibration, it can be proposed the value 0.091 [d^{-1}] for the BOD_5 biodegradation rate constant (K). Similar value 0.8 [d^{-1}] has observed from other researchers (R.Khusravi *et al*, 2013) in a stabilization pond system in Birjand a city in the East Iran.

The rate constant (K) has a very strong relationship with HRT (R^2 = 0.9999**)** expressed as the following equation:

$$K = 0.3579 – 0.004d \tag{6}$$

Where d is the HRT in days. For another expression of BOD_5 biodegradation rate constant (K) the value 3.67 *$g\ BOD_5\ m^{-2}d^{-1}$* is suggested. In this case the relationship that correlate (K) and HRT is as following with R^2 = 0.9522

$$K = 11.438 - 0.1258\ d \tag{7}$$

4. Conclusions

Even the terms of climate and hydrology are the same, the WSP systems have different characteristics and behavior, as their operation is multiparametric and their nature is a complex ecological system. The Kickuth Equation, which used typically in the design of stabilization ponds, showed a good mathematical relationship between theoretical predicted results and real data. According this equation it can be proposed BOD_5 biodegradation rate constant (K) equal to 0.091 d^{-1}. This constant K has a very strong relationship (R^2 = 0.9999) with hydraulic retention time (HRT) expressed as K = 0.3579 – 0.004d, where d is the HRT in days**.**

REFERENCES

1. Breen P.F. (1990), A mass balance method for assessing the potential of artificial wetlands for wastewater treatment. Water Research, 24 (6), 689-697.
2. Chalatsi M. (2014), Qualitative and hydrodynamics characteristic of stabilization pond systems in Northern Greece, PhD Thesis, Department of Civil Engineering, Democritus University of Thrace**.**
3. Chlot, S., Widerlund, A., Siergieiev, D., Ecke, F., Husson, E., & Öhlander, B. (2011). Modelling nitrogen transformations in waters receiving mine effluents. *Science of the Total Environment*, *409*(21), 4585-4595.
4. Gil Penha-Lopes , Mogens R. Flindt, Bo Ommen, Erik Kristensen, Pedro Garret, José Paula,(2012), Organic carbon dynamics in a constructed mangrove wastewater wetland populated with benthic fauna: A modelling approach**,** Ecological Modelling Vol. 232, 10 May 2012, Pages 97–108
5. Heliotis F.D. and DeWitt C.B. (1983). A conceptual model of nutrient cycling in wetlands used for wastewater treatment: A literature analysis. Wetlands, 3 (1), 134-152.

6. Howard-Williams C. (1985), Cycling and retention of nitrogen and phosphorus in wetlands: A theoretical and applied perspective. Freshwater Biology, 15 (4), 391-431.
7. IWA (2000), Constructed Wetlands for Pollution Control: Processes, Performance, Design and Operation. Scientific and technical Report No.8, IWA Publishing, London, UK.
8. Kadlec R.H. and Knight R.L. (1996), Treatment Wetlands. Lewis Publishers, CRC Press, Boca Raton, Florida.
9. Kayombo S., T.S.A. Mbwette, J.H.Y Katima N. Ladegaard, S.E. Jørgensen (2005), Waste Stabilization ponds and Constructed Wetlands Design Manual, IWA Publising.
10. Kayombo S., T.S.A. Mbwette, J.H.Y Katima, S.E. Jørgensen (2003), Effects of substrate concentrations on the growth of heterotrophic bacteria and algae in secondary facultative ponds, Water Research, Volume 37, Issue 12, July 2003, p.p 2937–2943
11. Korkusuz E.A. (2004), Domestic wastewater treatment in pilot-scale constructed wetlands implemented in the Middle East Technical University. Ph.D. Thesis, Department of Biotechnology, School of Natural and Applied Sciences, Middle East Technical University.
12. Krouse P., D.P.Boyle, and F.Bäse (2005), Comparison of different efficiency criteria for hydrologicl model assessment, Advances in Geosciences,5, 89-97, 2005.
13. Kuo J. (2014), Practical Design Calculations for Groundwater and Soil Remediation. Chapter 4: Mass-Balance Concept and Reactor Design, 2nd ed., Taylor & Francis Group, LLC, CRC Press, Boca Raton, Florida, 113-150.
14. Panikov Nikolai S. (2000), Microbial Growth Kinetics, 2nd Ed. Chapman &Hall
15. Rasoul Khusravi, Maryam Khodadadi, Abdolmajid Gholizadeh, Ehsan Abouee Mehrizi, Taher Shahriary and Abdoljavad Shahnia (2013), BOD_5 removal kinetics and wastewater flow pattern of stabilization pond system in Birjand, European Journal of Experimental Biology, 2013, 3(2):430-436
16. Ronnie A. D. Frazer-Williams (2010), Areview of the influence of Design parameters on the performance of constructed wetlands, Journal of Chemical Engineering, IEB Vol. ChE. 25, No. 1, December 2010, 29
17. Thornthwaite, C.W. (1948), An approach toward a rational classification of climate Geographical Review, v. 38, p. 55–94.
18. Tilley E. Urlich L, Leuethi C., Reymond P., Zurbruegg C. (2014), Waste Stabilisation Ponds, Swiss Federal Institute of Aquatic Science and Technology, http://www.sswm.info/category/implementation-tools/wastewater-treatment/hardware/
19. Zwietering, M. H., I. Jongenburger, F. M. Rombouts, and K.van 't Riet. (1990), Modeling of the bacterial growth curve. Appl.Environ. Microbiol. 56:1875-1881