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, Koné 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 $\phi$: $41^\circ$ up to $41^\circ15'$, longitude $\lambda$: $23^\circ21'$ up to $23^\circ36'$ and altitude from $14$m 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 1$^{st}$ 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-Sutcliffe 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 characteristics, 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 BOD₅ removal kinetics of three full –scale WSPs systems situated in the North part of Greece, treated municipal wastewater, as the removal of organic matter (BOD₅) 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, Chlott 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 [m³/d], A is the pond area [m²] 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.

\[ K_1 = \frac{Q}{A} \ln(C_{in} - C_{out}) \]  \hspace{1cm} \text{[m d⁻¹]}  \hspace{1cm} (1)

CEST2015_00622
The combined model of first order and CSTR gives the following simple equation:

\[ K = \frac{Q(C_{\text{in}} - C_{\text{out}})}{A(C_{\text{out}})} \quad \text{[m d\(^{-1}\)]} \]  \hspace{1cm} (2)

From the combination of Plug flow model and Monod equation \( \frac{dc}{dt} = k_{\text{max}} \frac{C}{C + C_{\text{na}}}, \) the following equation (Eq. 3) is derived under the consideration that \( k_{\text{max}} \) 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} \left( C_{\text{in}} - C_{\text{out}} \right) + 60 \ln \left( \frac{C_{\text{in}}}{C_{\text{out}}} \right) \quad \text{[g BOD\(_5\) m\(^{-2}\)d\(^{-1}\)]} \]  \hspace{1cm} (3)

Where \( k_{\text{max}} \) is the maximum BOD\(_5\) removed in WSPs regardless the effect of temperature [g/m\(^3\).d], \( C_{\text{na}} \) is the amount of wastewater BOD\(_5\) while the removed BOD\(_5\) value is half of \( k_{\text{max}} \). 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 \( k_{\text{max}} \).

\[ K_4 = \frac{Q}{A} \left( C_{\text{in}} - C_{\text{out}} \right) \left( 60 + C_{\text{in}} \right) \quad \text{[g BOD\(_5\) m\(^{-2}\)d\(^{-1}\)]} \]  \hspace{1cm} (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_{\text{in}} - C^*}{C_{\text{out}} - C} \right) \quad \text{[m d\(^{-1}\)]} \]  \hspace{1cm} (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\(_{\text{in}}\).

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\(_{\text{BOD}}^5\)” is being obtained both as calibration from linear regression and as the median of predicted values.

2.3. Statistical Analysis

The models denominated by Equations 1 to 5 were evaluated by comparing the real observed values \( F \) (C\(_{\text{in}}, C_{\text{out}}\)) 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
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-Sutcliffe efficiency $E$. The range of $E$ lies between 1.0 (perfect fit) and $-\infty$. 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 $\sigma$ to the mean $\mu$. 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 discussion

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)

<table>
<thead>
<tr>
<th>Equation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{BOD}$</td>
<td>0.065303</td>
<td>0.014184</td>
<td>1.312474</td>
<td>1.512003</td>
<td>0.012090</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.866216</td>
<td>0.866217</td>
<td>0.899738</td>
<td>0.874033</td>
<td>0.866217</td>
</tr>
<tr>
<td>$E$</td>
<td>0.860286</td>
<td>0.857351</td>
<td>0.893614</td>
<td>0.886338</td>
<td>0.768457</td>
</tr>
<tr>
<td>$CV$</td>
<td>0.056434</td>
<td>0.270267</td>
<td>0.147316</td>
<td>0.184373</td>
<td>0.234008</td>
</tr>
<tr>
<td>$R^2$ (K vs % removal)</td>
<td>0.986000</td>
<td>0.973100</td>
<td>0.752800</td>
<td>0.906700</td>
<td>0.976000</td>
</tr>
<tr>
<td>Median</td>
<td>0.064720</td>
<td>0.016530</td>
<td>1.326560</td>
<td>1.597190</td>
<td>0.013695</td>
</tr>
<tr>
<td>STD</td>
<td>0.003673</td>
<td>0.004294</td>
<td>0.193348</td>
<td>0.292545</td>
<td>0.003098</td>
</tr>
<tr>
<td>MIN</td>
<td>0.055690</td>
<td>0.006546</td>
<td>0.822847</td>
<td>0.882650</td>
<td>0.006231</td>
</tr>
<tr>
<td>MAX</td>
<td>0.071789</td>
<td>0.023221</td>
<td>1.623317</td>
<td>2.006131</td>
<td>0.018674</td>
</tr>
</tbody>
</table>

### Table 2: Stabilization Ponds of Vamvakofito – BOD$_5$ biodegradation rate constant (K)

<table>
<thead>
<tr>
<th>Equation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{BOD}$</td>
<td>0.082510</td>
<td>0.027763</td>
<td>2.922987</td>
<td>3.668164</td>
<td>0.019799</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.779028</td>
<td>0.773289</td>
<td>0.771706</td>
<td>0.685787</td>
<td>0.773289</td>
</tr>
<tr>
<td>$E$</td>
<td>0.959798</td>
<td>0.859390</td>
<td>0.407023</td>
<td>0.795733</td>
<td>0.771296</td>
</tr>
<tr>
<td>$CV$</td>
<td>0.044692</td>
<td>0.182621</td>
<td>0.145760</td>
<td>0.154181</td>
<td>0.131276</td>
</tr>
<tr>
<td>$R^2$ (K vs % removal)</td>
<td>0.985300</td>
<td>0.987100</td>
<td>0.351800</td>
<td>0.621000</td>
<td>0.989000</td>
</tr>
<tr>
<td>Median</td>
<td>0.090723</td>
<td>0.027198</td>
<td>2.916601</td>
<td>3.566146</td>
<td>0.019482</td>
</tr>
<tr>
<td>STD</td>
<td>0.004056</td>
<td>0.005176</td>
<td>0.426054</td>
<td>0.550280</td>
<td>0.002632</td>
</tr>
<tr>
<td>MIN</td>
<td>0.080730</td>
<td>0.018759</td>
<td>1.957796</td>
<td>2.336043</td>
<td>0.014915</td>
</tr>
<tr>
<td>MAX</td>
<td>0.097913</td>
<td>0.038225</td>
<td>3.824957</td>
<td>4.762412</td>
<td>0.025224</td>
</tr>
</tbody>
</table>

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$^{-1}$].
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 BOD₅ 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 (R² = 0.9999) expressed as the following equation:

\[
K = 0.3579 - 0.004d
\]

(6)

Where d is the HRT in days. For another expression of BOD₅ biodegradation rate constant (K) the value 3.67 g BOD₅ m² d⁻¹ is suggested. In this case the relationship that correlate (K) and HRT is as following with R² = 0.9522

\[
K = 11.438 - 0.1258d
\]

(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 BOD₅ biodegradation rate constant (K) equal to 0.091 d⁻¹. This constant K has a very strong relationship (R² = 0.9999) with hydraulic retention time (HRT) expressed as K = 0.3579 – 0.004d, where d is the HRT in days.

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CEST2015_00622