COD AND TSS REMOVAL REACTION RATE CONSTANT OF WASTEWATER STABILIZATION POND SYSTEMS IN N. GREECE

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Waste Stabilization Ponds (WSPs)

- Removal of organic matter, pathogenic organisms, nutrients and heavy metals
- Simple in terms of engineering and construction, but complex as ecological systems
- A lot of empirical models and design tools developed and used on-site in many countries
- Different characteristics in terms of climate and hydrology can lead to problems, when transferred without appropriate modifications to the local conditions
- A “uniform” simple method in all countries can cause malfunctions or reduced efficiency of WSP systems
- A great number of kinetic models for the biomass growth processes in the wastewater treatment literature
- Most of them without considering the consumption of substrate
- Little information about the dynamics of pollutants in WSP systems

- Zwietering et al. (1990): modified mathematical relationship (based on the Gompertz model) for the increase in biomass over time
  - Relates the population size over time to the specific growth rate, lag time and asymptotic level of organisms
  - TSS, COD, BOD and N-NH$_4^+$ used as substrate for evaluation, under the assumption that the removal was exclusively due to aerobic biodegradation
Greece

WSPs
- Only a few WSPs in Greece
- Just 8% of all Urban Wastewater Treatment Plants in the country
- 90% of them situated in North Greece
- Serving 500-4000 e.p. in rural regions
- 76% of them in the region of Serres
- Insufficient information

Present study
3 full scale WSPs monitored for 3 years:
✓ Charopo
✓ Vanvakofito
✓ N. Skopos

Objectives of the study
✓ Determination of TSS and COD bio-degradation rate constant $K_T$
✓ Optimization of design considerations and sizing requirements, according to the local conditions
✓ Determination of the suitability and the usefulness of different models, either available at the literature or newly developed
Layouts of the three systems as they were constructed

- **CHAROPO**
  - Lowland areas, with latitude $\phi$: 41° up to 41° 15′ B
  - Longitude $\lambda$: 23° 21′ up to 23° 36′ A
  - Altitude 14 up to 52 m
  - Mean monthly air temperature 4 – 29 °C
  - One facultative and one (N. Skopos) or two (Vamvakofito, Charopo) maturation ponds in series
  - Rock filter before the final discharge for algae filtration
  - Wastewater discharge through an open channel of 0.75 m$^2$ vertical section

- **VAMVAKOFITO**

- **N. SKOPOS**
Charopo

facultative pond

1st maturation pond

2nd maturation pond
Vamvakofito

facultative pond

1st maturation pond

2nd maturation pond
N. Skopos

facultative pond

maturation pond

connection of the 2 ponds
Dimensions, HRT and loading rates of the three systems (Current situation)

<table>
<thead>
<tr>
<th>WSP system</th>
<th>Charopo</th>
<th>Vamvakofito</th>
<th>N. Skopos</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inflow (m³/d)</td>
<td>137</td>
<td>121</td>
<td>152</td>
</tr>
<tr>
<td>HRT (d)</td>
<td>72.4</td>
<td>68.7</td>
<td>18.6</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>F: 0.80 – 2.40</td>
<td>F: 1.00 – 2.40</td>
<td>F: 0.75 – 2.40</td>
</tr>
<tr>
<td></td>
<td>M: 0.70 – 1.50</td>
<td>M: 0.75 – 1.50</td>
<td>M: 0.70 – 1.50</td>
</tr>
<tr>
<td>Area (m²)</td>
<td>7415</td>
<td>6016</td>
<td>2112</td>
</tr>
<tr>
<td>Volume (m³)*</td>
<td>9921</td>
<td>8311</td>
<td>2827</td>
</tr>
<tr>
<td>m³/e.p.</td>
<td>9.4</td>
<td>8.9</td>
<td>2.4</td>
</tr>
<tr>
<td>m²/e.p.</td>
<td>7.0</td>
<td>6.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

- Different characteristics at every system
- First operation of Charopo’s system in 1994
  of N. Skopos’s system in 1980
  of Vamvakofito’s system in 1989
- Instantaneous samples 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 the same morning period
- Meteorological data were recorded
- Samples in bottles of polyethylene 1000 mL
- Immediate transfer to the wastewater laboratory of Serres city
- Analysis with the methods proposed by the Simplified Laboratory Procedures for Wastewater Examination
- Inflow – outflow rates measured with handheld electromagnetic flow meter (constant supply during the day)
Materials and methods

✓ Mass balance method
  • Correction of the outflow data with the mass balance method
  • Elimination of errors from atmospheric precipitation and evapotranspiration

\[
\text{mass accumulation} = \text{mass input} - \text{mass output} \pm \text{mass generation or mass consumption}
\]

✓ Principle of mass conservation in a closed system

\[
Q_{\text{out}} = Q_{\text{in}} + I - \text{PET}
\]

\(Q_{\text{out}}\) = wastewater outflow quantity \([m^3/d]\)

\(Q_{\text{in}}\) = wastewater inflow quantity \([m^3/d]\)

\(I\) = water inflow quantity via precipitation \([m^3/d]\)

\(\text{PET}\) = water quantity lost via evapotranspiration \([m^3/d]\)

\(\Delta H = H_{\text{rain}} - H_{\text{PET}}\)

\(\Delta V = \Delta H \times A\)

\(\Delta V/d = Q' = Q - \Delta V/d\)

\(H_{\text{rain}}\) = Hellenic Meteo Service

\(H_{\text{PET}}\) = Thornthwaite method

\(\Delta H\) = \(H_{\text{rain}}\) - \(H_{\text{PET}}\)

\(\Delta V\) = \(\Delta H \times A\)

\(\Delta V/d\) = \(Q' = Q - \Delta V/d\)
**Kinetic models**

- **Combined model of first-order and plug flow** (first proposed by Kickuth)

  Widely used for sizing of HSF domestic sewage treatment

  \[
  K_1 = \frac{Q}{A} \ln \left( \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{out}}} \right) \quad \text{[m/d]}
  \]

  \(K\) = first-order kinetic constant for organic pollutant removal [m/d]

  \(Q\) = flow rate [m³/d]

  \(A\) = pond area [m²]

  \(C_{\text{in}}\) = input pollutant concentration [mg/L]

  \(C_{\text{out}}\) = output pollutant concentration [mg/L]

- **Combined model of first-order and CSTR (Continuous flow Stirred Tank Reactors)**

  \[
  K_2 = \frac{Q}{A} \times \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{out}}} \quad \text{[m/d]}
  \]

- **Global first-order substrate removal model for complete mixed system**

  \[
  K_3 = \frac{C_{\text{in}} - C_{\text{out}}}{\theta_H \times C_{\text{out}}} \quad \text{[d⁻¹]}
  \]

  \(\theta_H\) = hydraulic retention time (HRT) [days]

- **Stover – Kincannon model**

  The substrate utilization rate expressed as function of the organic loading rate by monomolecular kinetic for biofilm reactors (biological filters and moving bed biofilm reactors)

  \[
  K_B = \left( \frac{\theta_H}{C_{\text{in}} - C_{\text{out}}} - \frac{1}{U_{\text{max}}} \right) \times C_{\text{in}} \times U_{\text{max}} \quad \text{[g/L/d]}
  \]

  \(U_{\text{max}}\) = maximum substrate removal rate [mg COD/L/d]
Kinetic models

✓ $K - C^*$ model (developed by Kadlec and Knight for wetlands)

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

$K_5$ = first-order kinetic constant  [m/d]
$C^*$ = non-zero background  [mg/L]

$C^* = 3.5 + 0.0053 \, C_{in}$ for COD
$C^* = 5.1 + 0.160 \, C_{in}$ for TSS

• Combination of the basic equation of the plug flow model and the aqueous mass balance
• Differs from the original Kickuth equation in two ways
  − Reversible first-order reaction equation
  − Non-zero substrate concentration
• Describes better the removal of pollutants, as they cannot be reduced to zero, due to the release of pollutants into the treated water
• Developed for wetlands – similar characteristics with the examined WSP systems:
  − No sludge removal throughout the years of operation
  − Significant growth of self-sown reeds at the banks of the ponds
Statistic analysis

✓ Evaluation of the models’ performance with efficiency criteria

**Coefficient of determination** $r^2$ (squared value of the coefficient of correlation according to Bravais-Pearson)

- A measure of how well the observed outcomes are replicated by the model, as the proportion of the total variation of the outcomes explained by the model

- $r^2 = 0$  no correlation

- $r^2 = 1$  the dispersion of the prediction equal to that of the observation

**Nash-Sutcliffe efficiency** $E$

- $E = 1.0$  perfect fit

- $E = 0$  model predictions as accurate as the mean of the observed data

- $E < 0$  the observed mean a better predictor than the model

**Unitized risk or coefficient of variation** CV (ratio of the standard deviation $\sigma$ to the mean $\mu$)

- Extent of variability in relation to the mean of the population

- The closer to zero the better the fit
### WSPs of Charopo – COD biodegradation rate constant K (removal 46%)

<table>
<thead>
<tr>
<th>Equation</th>
<th>1 ($md^{-1}$)</th>
<th>2 ($md^{-1}$)</th>
<th>3 ($d^{-1}$)</th>
<th>4 ($g L^{-1}d^{-1}$)</th>
<th>5 ($md^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{TSS}$</td>
<td>0.0808</td>
<td>0.0161</td>
<td>0.0774</td>
<td>27.9845</td>
<td>0.0121</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.9270</td>
<td>0.9212</td>
<td>0.6250</td>
<td>0.8534</td>
<td>0.9212</td>
</tr>
<tr>
<td>$E$</td>
<td>0.9363</td>
<td>0.9262</td>
<td>0.7528</td>
<td>0.9570</td>
<td>0.8828</td>
</tr>
<tr>
<td>CV</td>
<td>0.0512</td>
<td>0.2108</td>
<td>0.8938</td>
<td>0.3874</td>
<td>0.1706</td>
</tr>
<tr>
<td>Median</td>
<td>0.0818</td>
<td>0.0160</td>
<td>0.5820</td>
<td>25.9313</td>
<td>0.0128</td>
</tr>
<tr>
<td>STD</td>
<td>0.0041</td>
<td>0.0034</td>
<td>0.9522</td>
<td>9.5863</td>
<td>0.0022</td>
</tr>
<tr>
<td>MIN</td>
<td>0.0741</td>
<td>0.0096</td>
<td>0.1368</td>
<td>10.2163</td>
<td>0.0085</td>
</tr>
<tr>
<td>MAX</td>
<td>0.0880</td>
<td>0.0224</td>
<td>3.9478</td>
<td>47.2700</td>
<td>0.0169</td>
</tr>
</tbody>
</table>

### Combined model of first-order and plug flow (Kickuth) [1]

- Best results for $K_{COD}$

<table>
<thead>
<tr>
<th>System</th>
<th>$K_{COD}$</th>
<th>$K_{B-COD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charopo</td>
<td>0.0808 m/d</td>
<td>27.9845 g COD/L/d</td>
</tr>
<tr>
<td>Vamvakofito</td>
<td>0.0993 m/d</td>
<td>22.4078 g COD/L/d</td>
</tr>
<tr>
<td>N. Skopos</td>
<td>0.2492 m/d</td>
<td>25.65 g COD/L/d</td>
</tr>
</tbody>
</table>

### Suggested values for the three systems

- $K_{COD} = 0.088$ m/d
- $K_{B-COD} = 25.20$ g COD/L/d
- $r^2 > 0.85$, $E > 0.83$, $58$ mg/L $\leq$ COD$_{in}$ $\leq$ 301 mg/L

### WSPs of Vamvakofito – COD biodegradation rate constant K (removal 69%)

<table>
<thead>
<tr>
<th>Equation</th>
<th>1 ($md^{-1}$)</th>
<th>2 ($md^{-1}$)</th>
<th>3 ($d^{-1}$)</th>
<th>4 ($g L^{-1}d^{-1}$)</th>
<th>5 ($md^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{TSS}$</td>
<td>0.0993</td>
<td>0.0349</td>
<td>0.1817</td>
<td>22.4078</td>
<td>0.0229</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.8553</td>
<td>0.8389</td>
<td>0.2357</td>
<td>0.4090</td>
<td>0.8389</td>
</tr>
<tr>
<td>$E$</td>
<td>0.9767</td>
<td>0.8530</td>
<td>0.2749</td>
<td>0.4894</td>
<td>0.8314</td>
</tr>
<tr>
<td>CV</td>
<td>0.0531</td>
<td>0.1572</td>
<td>0.9000</td>
<td>0.4265</td>
<td>0.1068</td>
</tr>
<tr>
<td>Median</td>
<td>0.0991</td>
<td>0.0351</td>
<td>1.0832</td>
<td>33.7538</td>
<td>0.0231</td>
</tr>
<tr>
<td>STD</td>
<td>0.0052</td>
<td>0.0055</td>
<td>1.6872</td>
<td>13.5981</td>
<td>0.0024</td>
</tr>
<tr>
<td>MIN</td>
<td>0.0861</td>
<td>0.0220</td>
<td>0.1704</td>
<td>10.1372</td>
<td>0.0168</td>
</tr>
<tr>
<td>MAX</td>
<td>0.1062</td>
<td>0.0503</td>
<td>6.9358</td>
<td>59.5981</td>
<td>0.0296</td>
</tr>
</tbody>
</table>

### WSPs of N. Skopos – COD biodegradation rate constant K (removal 39%)

<table>
<thead>
<tr>
<th>Equation</th>
<th>1 ($md^{-1}$)</th>
<th>2 ($md^{-1}$)</th>
<th>3 ($d^{-1}$)</th>
<th>4 ($g L^{-1}d^{-1}$)</th>
<th>5 ($md^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{TSS}$</td>
<td>0.2492</td>
<td>0.0384</td>
<td>0.0448</td>
<td>25.65037</td>
<td>0.0346</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.8058</td>
<td>0.8058</td>
<td>0.6310</td>
<td>0.7429</td>
<td>0.8058</td>
</tr>
<tr>
<td>$E$</td>
<td>0.9784</td>
<td>0.7535</td>
<td>0.7213</td>
<td>0.9149</td>
<td>0.7636</td>
</tr>
<tr>
<td>CV</td>
<td>0.1087</td>
<td>0.3154</td>
<td>1.0969</td>
<td>0.3701</td>
<td>0.2498</td>
</tr>
<tr>
<td>Median</td>
<td>0.2345</td>
<td>0.0365</td>
<td>0.2033</td>
<td>28.1108</td>
<td>0.0341</td>
</tr>
<tr>
<td>STD</td>
<td>0.0265</td>
<td>0.0116</td>
<td>0.4045</td>
<td>10.0037</td>
<td>0.0083</td>
</tr>
<tr>
<td>MIN</td>
<td>0.2093</td>
<td>0.0203</td>
<td>0.0431</td>
<td>7.5223</td>
<td>0.0199</td>
</tr>
<tr>
<td>MAX</td>
<td>0.3163</td>
<td>0.0695</td>
<td>1.6547</td>
<td>48.3079</td>
<td>0.0545</td>
</tr>
</tbody>
</table>

### Other researchers

- $0.06$ m/d, $23.81$ g COD/L/d

### Very strong relationship between $K_{COD}$ and HRT

- $K_{COD} = 0.3066 – 0.0031$ d ($R^2 = 0.9985$)
### WSPs of Charopo – TSS biodegradation rate constant K (removal 17%)

<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\textsubscript{TSS}</td>
<td>0.0360</td>
<td>0.0022</td>
<td>0.0106</td>
<td>6.9107</td>
<td>0.028</td>
</tr>
<tr>
<td>r\textsuperscript{2}</td>
<td>0.9470</td>
<td>0.9621</td>
<td>0.8565</td>
<td>0.9716</td>
<td>0.9621</td>
</tr>
<tr>
<td>E</td>
<td>0.6262</td>
<td>0.9510</td>
<td>0.9607</td>
<td>0.9995</td>
<td>0.9351</td>
</tr>
<tr>
<td>CV</td>
<td>1.0766</td>
<td>0.6645</td>
<td>1.0956</td>
<td>2.5161</td>
<td>0.7131</td>
</tr>
<tr>
<td>Median</td>
<td>0.0349</td>
<td>0.0042</td>
<td>0.0400</td>
<td>4.1976</td>
<td>0.0054</td>
</tr>
<tr>
<td>STD</td>
<td>0.0279</td>
<td>0.0025</td>
<td>0.0760</td>
<td>541.37</td>
<td>0.0040</td>
</tr>
<tr>
<td>MIN</td>
<td>0.0184</td>
<td>1.85x10\textsuperscript{-5}</td>
<td>0.0010</td>
<td>1.3423</td>
<td>2.38x10\textsuperscript{-5}</td>
</tr>
<tr>
<td>MAX</td>
<td>0.0487</td>
<td>0.0082</td>
<td>0.3260</td>
<td>1626.74</td>
<td>0.0141</td>
</tr>
</tbody>
</table>

### Combined model of first-order and CSTR [2]

- **Kadlec and Knight model [5]**
  - Good mathematical relationship between theoretical predicted results and site TSS data

- **Stover-Kincannon model [4]**
  - Good results for \( K_{B-TSS} \)

### WSPs of Vamvakofito – TSS biodegradation rate constant K (removal 60%)

<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\textsubscript{TSS}</td>
<td>0.0713</td>
<td>0.0263</td>
<td>0.1263</td>
<td>28.2379</td>
<td>0.0270</td>
</tr>
<tr>
<td>r\textsuperscript{2}</td>
<td>0.8258</td>
<td>0.8415</td>
<td>0.4293</td>
<td>0.7620</td>
<td>0.8375</td>
</tr>
<tr>
<td>E</td>
<td>0.2202</td>
<td>0.8057</td>
<td>0.4522</td>
<td>0.8922</td>
<td>0.7942</td>
</tr>
<tr>
<td>CV</td>
<td>0.1103</td>
<td>0.2836</td>
<td>0.9957</td>
<td>0.4006</td>
<td>0.2921</td>
</tr>
<tr>
<td>Median</td>
<td>0.0693</td>
<td>0.0246</td>
<td>0.2141</td>
<td>12.1925</td>
<td>0.0266</td>
</tr>
<tr>
<td>STD</td>
<td>0.0077</td>
<td>0.0090</td>
<td>0.4317</td>
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<td>0.0088</td>
</tr>
<tr>
<td>MIN</td>
<td>0.0523</td>
<td>0.0136</td>
<td>0.0481</td>
<td>3.2822</td>
<td>0.0148</td>
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<tr>
<td>MAX</td>
<td>0.0878</td>
<td>0.0435</td>
<td>2.0238</td>
<td>21.0100</td>
<td>0.0502</td>
</tr>
</tbody>
</table>

### WSPs of N. Skopos – TSS biodegradation rate constant K (removal 37%)

<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\textsubscript{TSS}</td>
<td>0.1221</td>
<td>0.0378</td>
<td>0.0424</td>
<td>1.9245</td>
<td>0.0668</td>
</tr>
<tr>
<td>r\textsuperscript{2}</td>
<td>0.7523</td>
<td>0.7342</td>
<td>0.4474</td>
<td>0.6112</td>
<td>0.9613</td>
</tr>
<tr>
<td>E</td>
<td>0.8938</td>
<td>0.6998</td>
<td>0.7766</td>
<td>0.9661</td>
<td>0.6557</td>
</tr>
<tr>
<td>CV</td>
<td>0.1383</td>
<td>0.4427</td>
<td>0.9148</td>
<td>0.6063</td>
<td>0.4766</td>
</tr>
<tr>
<td>Median</td>
<td>0.1231</td>
<td>0.0379</td>
<td>0.0316</td>
<td>1.6613</td>
<td>0.0728</td>
</tr>
<tr>
<td>STD</td>
<td>0.0176</td>
<td>0.0185</td>
<td>0.0524</td>
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<td>0.0374</td>
</tr>
<tr>
<td>MIN</td>
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<td>0.0166</td>
<td>0.1816</td>
<td>0.1190</td>
<td>0.0304</td>
</tr>
<tr>
<td>MAX</td>
<td>0.3163</td>
<td>0.0981</td>
<td>1.6547</td>
<td>4.4709</td>
<td>0.2136</td>
</tr>
</tbody>
</table>

### Suggested values for the three systems

- **Charopo**
  - \( K_{TSS} = 0.0022 \text{ m/d} \)
  - \( K_{B-TSS} = 6.9107 \text{ g TSS/L/d} \)

- **Vamvakofito**
  - \( K_{TSS} = 0.0263 \text{ m/d} \)
  - \( K_{B-TSS} = 28.2379 \text{ g TSS/L/d} \)

- **N. Skopos**
  - \( K_{TSS} = 0.0668 \text{ m/d} \)
  - \( K_{B-TSS} = 1.9245 \text{ g TSS/L/d} \)

### For the system Charopo

- \( r^2 > 0.97 \quad E > 0.35 \quad 11 \text{ mg/L} \leq TSS_{in} \leq 105 \text{ mg/L} \)

### Very strong relationship between \( K_{TSS} \) and HRT

\[ K_{TSS} = 0.0867 - 0.001 \text{ d} \quad (R^2 = 0.9302) \]
Conclusions

- Different characteristics and behavior among the three systems, although the same climate and hydrology
  - $K_{\text{COD}} = 0.088 \text{ m/d}$
  - $K_{\text{B-COD}} = 25.20 \text{ g COD/L/d}$
  - $r^2 > 0.85$ for $58 \text{ mg/L} \leq \text{COD}_{\text{in}} \leq 301 \text{ mg/L}$

- Combined model of first-order and CSTR
  - Kadlec and Knight model
  - $K_{\text{COD}} = 0.0257 \text{ m/d}$
  - $K_{\text{B-COD}} = 12.2139 \text{ g TSS/L/d}$
  - $r^2 > 0.97$ for $11 \text{ mg/L} \leq \text{TSS}_{\text{in}} \leq 105 \text{ mg/L}$

- Very strong relationship between $K$ and HRT
  - $K_{\text{COD}} = 0.3066 - 0.0031 \text{ d} \ (R^2 = 0.9985)$
  - $K_{\text{TSS}} = 0.0867 - 0.001 \text{ d} \ (R^2 = 0.9032)$

- Application of the estimated parameters in WSP sizing in Mediterranean climatic conditions
Thank you for your attention