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# Modeling of Organic Substances and Ammonia Nitrogen Removal in Vertical Flow Constructed Wetlands

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**ABSTRACT**
The aim of the research was to determine the possibility of using and adapting regression models for a description of constructed wetland systems treating reject water from aerobic sewage sludge stabilization. The P-k-C* model was investigated along with related models. The research was carried out using reject water from aerobic sewage sludge stabilization in dairy wastewater treatment plant (WWTP) belonging to Mlekovita in Wysokie Mazowieckie. The main components of the research installation were two vertical flow constructed wetland beds with passive aeration operating at 0.1 m/d hydraulic load. The following parameters were used for modeling: $BOD_5$, COD, $N\text{-}NH_4^+$ and temperature. Air temperature was also monitored.

**Keywords:** treatment modeling, vertical flow constructed wetlands, reject water, organic substances, ammonia nitrogen

## INTRODUCTION

Most of the dairy plants located in Poland use individual wastewater treatment systems. This is due to the large load of wastewater discharged from the plants. Biological oxygen demand ($BOD^5$) in sewage from Podlaskie dairy WWTPs reaches up to 3000 $mg \cdot dm^{-3}$, while COD is up to 9000 $mg \cdot dm^{-1}$ [Wiater et al. 2019]. The activated sludge method is the most popular for municipal and industrial sewage treatment. Sewage sludge, as a by-product of wastewater treatment, is usually stabilized with separate aeration chambers. Anaerobic stabilization is applied only in the largest dairy WWTPs, its advantage is the possibility of producing biogas, which can be used to generate heat and electricity. In both cases of aerobic and anaerobic stabilization systems in municipal and industrial sewage treatment plants, reject water is formed, which largely affects the process of effective wastewater treatment [Janus & Van der Roast 1997, Fux et al. 2002, 2006].

This is particularly the result of ammonium nitrogen concentration in reject water, which, according to Gajewska and Obarska-Pempkowiak (2011), is up to 941 $N\text{-}NH_4^+ dm^{-3}$ in municipal WWTP with anaerobic sewage sludge stabilization, while the content of organic substance measured by COD or $BOD_5$ is similar to that observed in municipal sewage. In addition, they found an unfavorable $COD/BOD_5$ ratio in the reject water, which hinders the biological treatment process using a conventional activated sludge method. Intensive biological and chemical treatment processes, introduced in connection with the growing environmental requirements, lead to an increase in the amount of obtained sewage sludge requiring treatment and consequently to an increase in the load of the treatment plant by reject water. The reject waters are recycled to the main treatment process in Polish treatment plants. Their composition may be conditioned by the stabilization method and the type and quantity of chemical substances used during dewatering and thickening of sewage sludge.

Among the methods, that can be used to treat reject water in addition to classical nitrification and denitrification, unconventional methods such as: BABE (Bio-Augumentation Batch Enchanced), ANAMMOX process (Anaerobic Ammonia Oxidation), SHARON process (Single reactor system for High-rate Ammonia Removal Over Nitrite), CANON method (Completely Autothrophic Nitrogen Removal Over Nitrite), or the OLAND method (Oxygen-Limited Autothropic Nitrification-Denitrification) can be applied. The mentioned methods, with exception of SHARON, are at the stage of implementation research and probably not used in Poland due to high costs.

One of the alternative solution may be the use of constructed wetlands as a simple method which doesn't require the use of chemicals and is characterized by high efficiency and very low energy consumption. This method is commonly used for the treatment of domestic sewage, in the final stage of municipal sewage treatment or for very specific sewage as e.g. leachate from landfills or sewage from septage tanks [Wojciechowska & Warra 2011, Karolinczak & Dąbrowski 2017, Obarska-Pempkowiak et al. 2015]. Constructed wetland treatment is a biological process modeled on natural changes occurring in swampy environments with the participation of heterotrophic microorganisms and aquatic plants. The wetland system consists of properly designed filter beds with vertical or horizontal flows. An extensive root system enables proper sewage flow, ensures adequate oxygenation of the bed and prevents clogging of the bed. Research related to the use of wetland systems to treat reject water from municipal treatment plants or leachate landfills has been conducted in the last decade by researchers from the Gdańsk University of Technology. In turn, in the research center in Bialystok (Bialystok University of Technology) similar studies were conducted on the efficiency of the wetland systems for reject water treatment from both aerobic and anaerobic sludge stabilization in dairy WWTPs. The database of reject water parameters before and after the treatment process using subsurface vertical and horizontal (SS VF and SS HF) beds obtained in 2015–2016 enabled modeling of the process using the reject water temperature. The P-k-C* model was applied. Multimodel nonlinear segmented regression analysis was performed for estimation of final dependency parameters and their estimates [Dąbrowski et al. 2019].

The modeling process was carried out due to the large number of dairy WWTPs, which operate on the basis of aerobic sewage sludge stabilization. In addition to the scientific aspect, it is important that the results of modeling can be applied in practice by operators of existing facilities as well as the designers.

## RESEARCH INSTALLATION

The research installation used to obtain data for modelling consisted of two SS VF beds (A and B). It was operating in dairy WWTP in Wysokie Mazowieckie. Figure 1 presents the scheme of the research installation with basic parameters and sampling points (I-III) while figure 2 presents a bed cross section. Both beds were supplied with the same load 0.1 $m^3 \cdot m^{-2} \cdot d^{-1}$ (0.1 $md^{-1}$) of reject water from sedimentation and retention tanks. It allowed a comparison of efficiency of beds with different heights and filling structures (Table 1). Both beds were planted with reeds (*Phragmites australis*) and operating with passive aeration.

Figure 3 presents the scheme of dairy WWTP in Wysokie Mazowieckie along with the localization of the research installation (11). Reject water obtained during dewatering of aerobically

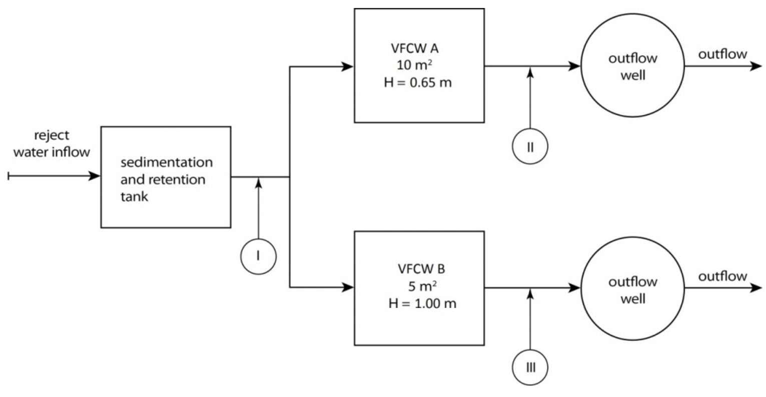


**Figure 1**. Research installation scheme, basic parameters along with sampling points (I, II, III)

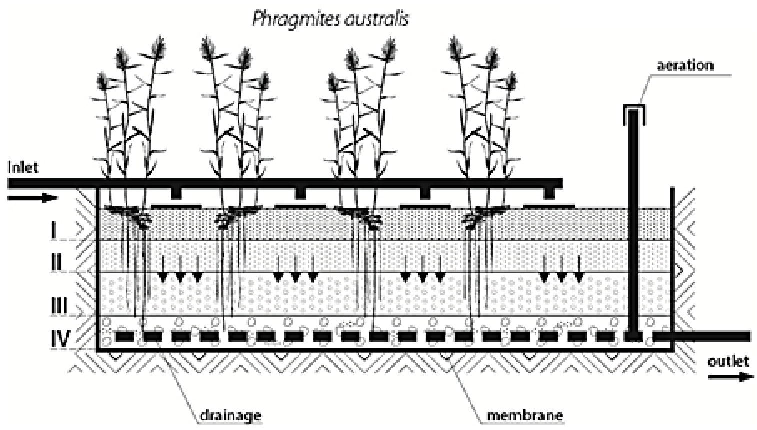


**Figure 2**. SS VF bed cross section.

stabilized sludge was supplying the sedimentation and retention tanks of the research installation (Figure 2).

## Sampling and scope of determination

The study was carried out between April 2015 and March 2016. A total of 38 measurement series were performed. Samples of raw reject water (sampling point I) and treated in SS VF beds A and B (sampling points II and III) were collected three times a month. The air temperature during the research period was monitored and also the temperature of reject water was measured. Air temperature varied from -15°C to 28°C while reject water temperature varied from 9°C to 28°C. The basic physical and chemical analyses were performed to analyze treatment efficiency: $BOD_5$, COD, total Kjeldahl nitrogen TKN, ammonia nitrogen $N\text{-}NH_4^+$, nitrate nitrogen (V) $N\text{-}NO_3^-$, nitrite nitrogen (III) $N\text{-}NO_2^-$, total phosphorus TP and dissolved oxygen. Unit loads in influent and effluent were used to calculate the removed load. Modeling of $BOD_5$, COD and $N\text{-}NH_4^+$ removal was performed using the P-k-C* model [Kadlec & Wallace 2009]. Determinations were conducted in a certified laboratory in accordance with the procedures set out in the Regulation of the Environmental Protection Minister on 18th November 2014 and in accordance with the American Public Health Association (2005). In situ measurements were performed using a multi-function weather station Velleman WS 1080 and WTW Multiline apparatus.

**Table 1**. SS VF bed cross section details

| Layer | Material | Bed "A" | Bed "B" |
|---|---|---|---|
| 1 | sand (0–2 mm) | 0.15 m | 0.30 m |
| 2 | gravel (2–8 mm) | 0.15 m | 0.25 m |
| 3 | gravel (8–20 mm) | 0.20 m | 0.30 m |
| 4 | gravel (20–80 mm) | 0.15 m | 0.15 m |

## METHODS

The P-k-C* model in form of was investigated for describing load removal of $BOD_5$, COD, $N\text{-}NH_4^+$.

$$1-\eta_{app} = \left(1+\frac{k(T)}{qP}\right)^{-P} \tag{1}$$

where: $\eta_{app}$ – apparent removal efficiency [–];
$k(T)$ – chemical reaction coefficient (temperature dependent);
$q$ – hydraulic load [m/d];
$P$ – total apparent number of tanks in series;

Apparent removal efficiency is defined as:

$$\eta_{app} = 1-\frac{C_{out}-C^*}{C_{in}-C^*} \tag{2}$$

where: $C_{out}$ – output concentration;
$C_{in}$ – input concentration; $C^*$ – total background concentration. All concentrations in [g/m$^3$].

Chemical reaction coefficient k(T) is modeled using first order temperature dependency with modification:

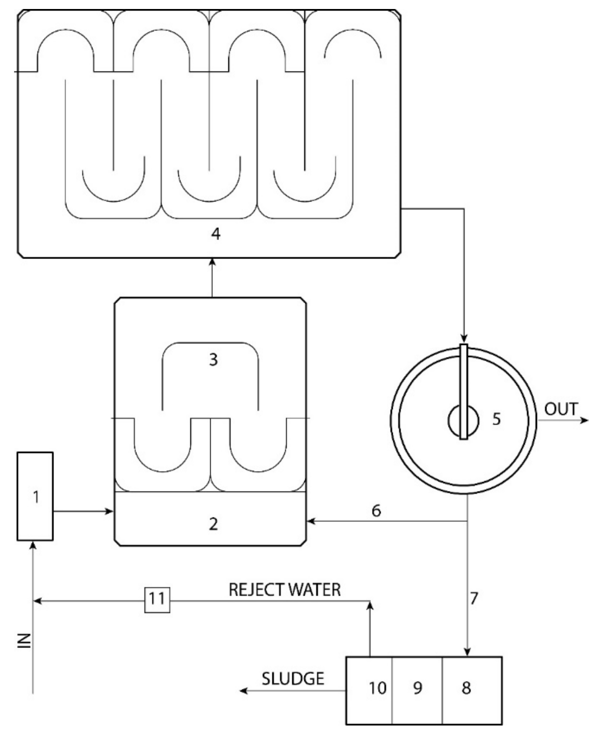


**Figure 3**. Dairy WWTP in Wysokie Mazowieckie. 1 – mechanical treatment; 2, 3, 4 – carbon and nutrients removal in sludge activated chambers; 5 – sedimentation tank, 6 – sludge recirculation; 7 – excess sludge; 8 – sewage sludge thickening; 9-sewage sludge aerobic stabilization; 10 – sewage sludge dewatering; 11 – research installation with two SS VF beds.

$$k(T) = K_{20}\theta^{T-20}\theta_m^{\min(T-T_k,0)}$$

$$\equiv \exp\Big(\ln K_{20} + [T-20]\ln\theta + \tag{3}$$

$$+\big[\min(T-T_k,0)\big]\ln\theta_m\Big)$$

where: $k(T)$ – chemical reaction coefficient;
$K_{20}$ – chemical reaction coefficient normalized for 20 [°C];
$\theta$ – temperature coefficient;
$\theta_m$ – modifier for temperature coefficient for temperatures less than critical temperature $T_k$, where trend changes;
*min (·,·)* – minimum function of 2 arguments.

Additional coefficient $\theta_m$ allows for a change of temperature dependency below certain temperature $T_k$, allowing for more flexibility in describing obtained data, while preserving first order dependency form.

Various simplifications to presented equations are possible. Apparent efficiency presented in model real efficiency η in limit $C^* \to 0$ . If ln $\theta_m = 0$, equation take form of ordinary first order dependency. When $P$ is very large, i.e. $P \to \infty$, proper limit can be taken:

$$\lim_{P\to\infty}\left(1+\frac{k(T)}{qP}\right)^{-P} = \exp\big(-k(T)/q\big) \tag{4}$$

Presented parameter space allows for 12 different temperature-dependent models to be built and evaluated on data, along with 4 models with no dependency. They can be estimated using non-linear reweighted least squares procedure with Levenberg-Marquardt's algorithm for optimization [Nash 1990]. To select a final form of model, methodology from [Burnham & Anderson 2002] was applied. Groups of nested models were created using differences $\Delta_i$ between second order [Sugiura, 1978] information criterion [Akaike, 1974], and weighted using Akaike weights $w_j$. Groups containing models that do not fulfill requirements of linear fit were further discarded.

Calculations were performed using R version 3.6.1 [R Code team, 2019]. Models' optimization was performed using nlfb procedure from nlsr package [Nash & Murdoch 2019]. AICc procedure from AICcmodavg package [Mazerolle 2019] was used for calculating second order information criterion.

## RESULTS

Table 2 presents the characteristics of reject water before and after treatment (sampling points I, II, III, Figure 1) with SS VF A and B beds during research period. The ratio of medians of $BOD_5$/COD was 0.55, while $BOD_5$/TN ratio was 2.67.

The multimodel analysis of data revealed existence of 3 groups of models for $BOD_5$ and N-$NH_4^+$. For COD there were 2 such groups. The first group captures more than 90% of Akaike weight among all groups analyzed, also residual diagnostic reveals non-symmetric residual structure for other groups of models. Therefore only the first group is preferred by data and present valid nonlinear fit. C* and P parameters do not sufficiently adjust the models to yield a substantially better fit. Models for $BOD_5$ and N-$NH_4^+$ have break points with constant removal efficiencies after a specific critical temperature. Data for COD removal supports the plug flow model as the simplest and best one in terms of fitness. Obtained models are presented in Figure 4. Table 3 presents the estimation of models parameters along with their confidence intervals.

**Table 2.** Characteristics of reject water

| Parameter | Sampling point I | Sampling point II | Sampling point III |
|---|---|---|---|
| $BOD_5$ | 120.0±13.3 | 14.00±2.96 | 11.00±4.44 |
| COD | 220.0±31.1 | 52.00±8.89 | 42.00±7.41 |
| N-$NH_4^+$ | 21.60±2.37 | 3.000±1.482 | 4.000± 1.482 |
| TN | 45.00±3.63 | 20.60±1.48 | 21.85±1.40 |
| TP | 9.050±2.594 | 5.900±1.186 | 4.850±0.444 |

**Note:** median±scaled median absolute deviation.

## DISCUSSION

The presented results showed that it is possible to remove main pollutants from reject water using wetland systems with high efficiency. The ratios of medians of $BOD_5$/COD (along with $BOD_5$/TN) give information about biodegradability. Low $BOD_5$/COD ratio pointed towards low degradability of the organic compounds. Reject water from dairy WWTP with aerobic sewage sludge stabilization was discovered to have a higher $BOD_5$/COD ratio than municipal WWTPs.

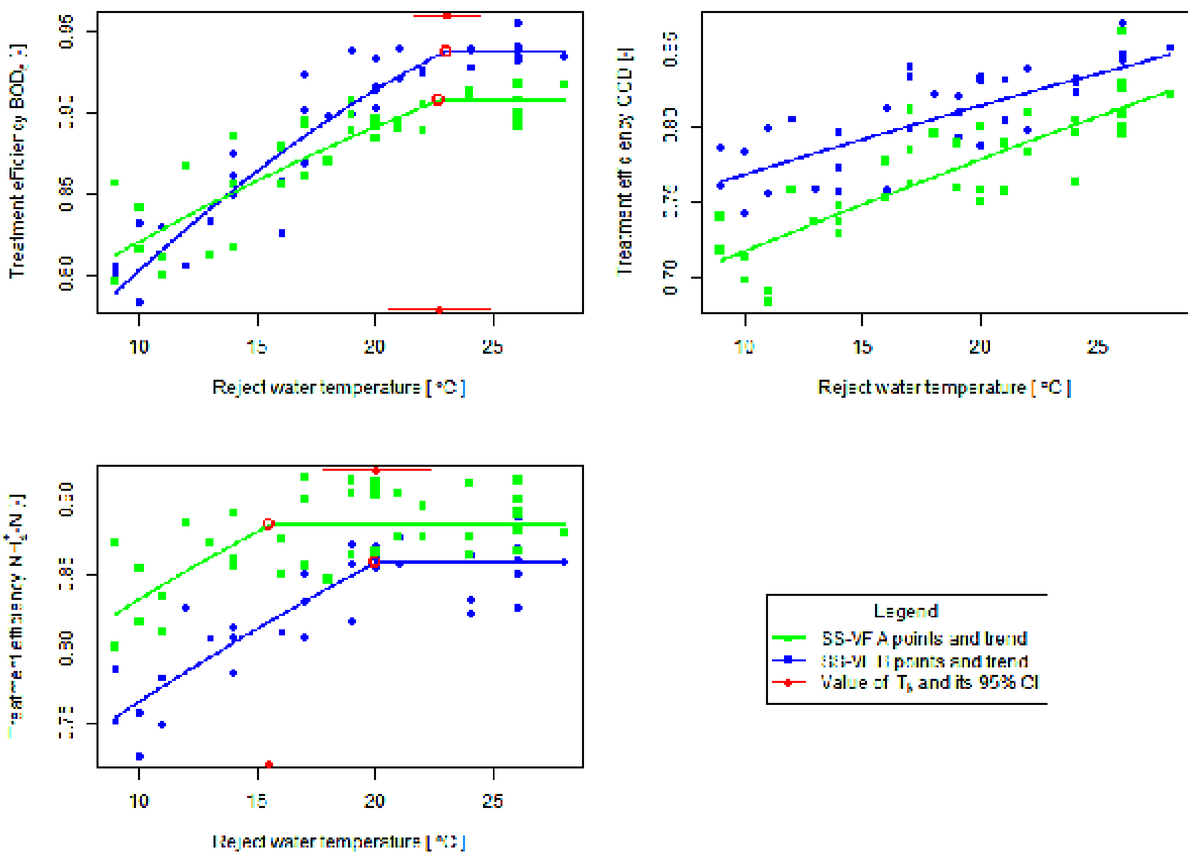


**Figure 4.** Obtained best models fit along with the data

**Table 3.** Parameters of selected models for $BOD_5$, COD and $N\text{-}NH_4^+$

| $BOD_5$ | | | | | | | |
|---|---|---|---|---|---|---|---|
| Bed A | | | | Bed B | | | |
| Parameter | Estimate/Value | Lower 95% CI | Upper 95% CI | Parameter | Estimate/Value | Lower 95% CI | Upper 95% CI |
| $T_k$ | 22.694 | 20.542 | 24.846 | $T_k$ | 23.005 | 21.58 | 24.431 |
| $\theta_m$ | 1.026 | 1.02 | 1.032 | $\theta_m$ | 1.042 | 1.036 | 1.049 |
| $K_{20}$ | 0.238 | 0.23 | 0.247 | $K_{20}$ | 0.278 | 0.269 | 0.289 |
| RSS | 0.78762 | - | | RSS | 1.0001 | - | |
| COD | | | | | | | |
| Bed A | | | | Bed B | | | |
| Parameter | Estimate/Value | Lower 95% CI | Upper 95% CI | Parameter | Estimate/Value | Lower 95% CI | Upper 95% CI |
| $\theta$ | 1.018 | 1.014 | 1.022 | $\theta$ | 1.014 | 1.01 | 1.018 |
| $K_{20}$ | 0.106 | 0.098 | 0.114 | $K_{20}$ | 0.127 | 0.118 | 0.136 |
| RSS | 0.59694 | -- | | RSS | 0.55575 | | |
| $N\text{-}NH_4^+$ | | | | | | | |
| Bed A | | | | Bed B | | | |
| Parameter | Estimate/Value | Lower 95% CI | Upper 95% CI | Parameter | Estimate/Value | Lower 95% CI | Upper 95% CI |
| $T_k$ | 15.534 | 11.55 | 19.519 | $T_k$ | 20.00 | 17.73 | 22.27 |
| $\theta_m$ | 1.033 | 1.003 | 1.065 | $\theta_m$ | 1.031 | 1.021 | 1.04 |
| $K_{20}$ | 0.215 | 0.208 | 0.222 | $K_{20}$ | 0.195 | 0.189 | 0.202 |
| RSS | 1.5156 | - | | RSS | 0.79303 | - | |

All obtained models confirm the temperature dependence of the treatment process, which is reflected in the estimated values of purification efficiency and is confirmed in the literature [Kadlec & Reddy 2001]. It is worth mentioning, however, that for almost the entire temperature range and regardless of the bed, the obtained efficiency was greater than 80% [$BOD_5$], 70% [COD] and 75% [$N\text{-}NH_4^+$] respectively and reached 95% [$BOD_5$], 85% [COD] and 90% [$N\text{-}NH_4^+$]. The B bed (deeper but with a smaller surface) was characterized by an increased temperature sensitivity to the "A" bed in $BOD_5$ removal, and almost identical sensitivity for COD and $N\text{-}NH_4^+$. Thus, it obtained better results in the removal of organic substances ($BOD_5$ and COD). In addition, a change in the nature of the temperature dependence for the biological oxygen demand and ammonia nitrogen was observed: above the specified temperature, the efficiency remained stable. This is due to the increased evaporation of the bed and the achievement of maximum efficiency of nitrification and denitrification processes, as a result from the ratio of nitrogen forms to carbon forms in the treated reject water.

The form of the final models of bed work is worth mentioning. The selected models clearly favor the plug-flow model of bed work [limit values of parameters C*, P]. Professional literature has long pointed out the need to include these parameters in the built models [Kadlec & Wallace 2009]. This may be due to insufficient samples. Not for the first time, however, the data shows insensitivity to the values of these parameters [Merriman et al. 2017]. This confirms, once again, the great difficulty in statistical analysis of beds using the P-k-C* method [Kadlec, 2000] and the need for special calculation methods.

The obtained results confirm the need for further research on the work of constructed wetlands and the possibility of their use in the treatment of impurities of various origin. Due to the low operating cost of such an installation, its aesthetics and environmental friendliness, the constructed wetland system is a good alternative to reject water treatment compared to industrial methods previously used.

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