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Technical attainment of real-time control system for industrial wastewater management

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ABSTRACT

Environmental protection is one of the today's most important concerns, therefore, firms are expected to reduce their environmental loads continuously whilst enhancing their productivity. In our study, a procedure was developed to manage the wastewater of a pharmaceutical process. The parameters of the wastewater, which flows into the sewerage system, are generally below the permitted threshold values, but occasionally exceed the limits. To improve this situation, online measuring equipment was deployed to estimate chemical oxygen demand (COD_{cr}) on the basis of the sugar content of an aqueous solution (BRIX) refractometric method. A mathematical model was developed for data processing and a control module was designed for the decisions. The measuring module was tested for 45 d. The data received were used for testing and monitoring the control module. During the test period it was found that the volume of the water requiring transfer for COD_{cr} removal fell by 50%, whilst no water with parameters above the threshold value flowed into the sewerage system.

Keywords: Real-time system; COD_{cr}; BRIX; Wastewater

1. Introduction

Nowadays, environmental protection is one of the most important concerns facing private individuals and industry. The principle of sustainable development continuously requires a reduction in the environmental load. The management of wastewater is a fundamental question in freshwater protection. So many studies deal with the development of this area [1–4] and there are strict orders controlling the parameters of the wastewater that flows into drains. In Hungary, the 2004 decree of the Ministry of Environmental Protection deals with the parameters of wastewater and sets the limits for pH, chemical oxygen demand (herein after COD_{cr} [mg/L, L]), biochemical oxygen demand, total nitrogen, total phosphorus, etc. [1]. In this study, we discuss a control system for wastewater management at a Hungarian pharmaceutical factory. This wastewater is channelled into the public sewer and its critical parameters are COD_{cr}, conductivity and pH. The COD_{cr} test measures the oxygen consumption during the oxidation process of the organic pollutants under standard conditions. The COD_{cr} limit depends on the drain type, but in this case it is 1,000 mg/L, which is usually adhered to, but was exceeded on a few occasions. If the COD_{cr} is above the threshold it needs to be transferred for further treatment and COD_{cr} removal [5,6].

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Using current technology, the wastewater is collected into three tanks, each with a volume of 24 m^3. The first tank equalises and adjusts the pH of the water. The outflowing water fills the next two tanks alternately. These tanks are connected in parallel. When a tank becomes full, its water is pumped into the drain, and the incoming water is collected in the other tank.

The difficulty in improving this system is that the COD_{cr} value cannot be measured online. Available instruments are expensive, complicated and comprise fragile apparatus with high working costs [7–9], but the main problem with them is that these analysers work based on measuring specific chemical reactions, and their working time is at least 6–10 min. It does not make a real-time response possible. The creation of a real-time control system requires online measurement techniques, which can measure a few parameters and make it possible to estimate the COD_{cr} value with precision (~100 mg/L) especially near the limit (1,000 mg/L). The pH measurement and adjustment have already been solved.

The final purpose is a dynamic wastewater assessment and management system, which can estimate the temporary COD_{cr} value of the water, the selection of the tank depending on this value, the water level of the tanks and the volume of the stream. The purpose is to minimise the volume of water which is above the COD_{cr} limit, and to maximise the mean COD_{cr} value of this portion of water. Minimising the volume above the limit decreases the cost of the transfer, furthermore, this cost is free for wastewater above a COD_{cr} of 10,000 mg/L because it can be used for methane production.

A mathematical model has been proposed [10,11], which calculates the COD_{cr} of the wastewater using data of online measurements. Details can be found here [11]. In this work, there is an analysis about the usability of this model with many industrial measurements on the basis of three water treatment technologies, which is designed to help in choosing the technology.

2. Calculation

2.1. Calibration curves

For a pure sugar solution there is a direct correlation between COD_{cr} (k) and the sugar content of an aqueous solution, BRIX (r refraction) with an $R^2 = 0.9950$ correlation coefficient. The wastewater contains other components with an effect on the refraction, besides the sugar; there, the relation between them will be stochastic with a lower ($R^2 = 0.5475$) correlation coefficient [10,11]. A better correlation can be gained ($R^2 = 0.6183$) by measuring resistance and establishing the corrected value of refraction (BRIX* [%])

$$r^* = r - 0.1\Omega \tag{1}$$

where Ω is the conductivity (mS/cm) [10]. The other parameters (pH and temperature, T) have not increased the value of R^2 [11], therefore, r and Ω can be regarded as optimal parameters.

COD_{cr} is a random variable κ, with a k (mg/L) mean value (in this case the most probable value) and σ (mg/L) standard deviation. The calibration curves [10,11], i.e., the dependence of the mean value (k) and standard deviation (σ) of COD_{cr} (calculated) on the corrected refraction (r^*), can be written in the following way [11]:

$$\ln\frac{k}{72000-k} = -6.05 + 1.09r^* + 0.2r^{*2} \tag{2}$$

$$\ln\frac{\sigma}{12500-\sigma} = -4.42 + 1.38r^* + 0.16r^{*2} \tag{3}$$

The standard deviation σ is of the same order as the mean value k. The $k \pm 2\sigma$ is the interval where the random variable κ has a probability of 95%. The lower value is practically 0, therefore, the upper (calculated) value must be given, which (with a 95% one-sided probability level) is as follows [11]:

$$k^+ = k + 1.64\sigma \tag{4}$$

The COD_{cr} threshold for the wastewater that has to be run into the drain is $k_{LIMIT} = 1{,}000$ mg/L, i.e., $k^+ \le k_{LIMIT}$. Since $k \cong \sigma$, k must be much smaller than 400 mg/L, so the COD_{cr} value that goes into the drain is much lower than permitted. The next solution can decrease the standard deviation [11].

2.2. Tank level

Let us assume the number of measurements is n and the tank inlet wastewater is Δl_i (l is the volume fraction, $l = 0$ if $j = 0$, and $l = 1$ if $j = n$) between the times t_i and $t_i - t_{i-1}$ for the ith measurement. The tank volume, the tank fullness until the jth measurement (until t_j time), is as follows:

$$l_j = \sum_{i=1}^{j} \Delta l_i = l \tag{5}$$

where $i \le j$.

2.3. Cumulative COD_{cr}

One way to decrease the standard deviation is by introducing the cumulative COD_{cr} [11], which is an integrated COD_{cr}, to the l_j tank level. The cumulative COD_{cr}, similar to κ, is a random variable, whose mean value of cumulative COD_{cr} has been defined as follows:

$$K_j = \sum_{i=1}^{j} k_i \Delta l_i \cong K_l \tag{6}$$

where $k_i = k(r_i^*)$. K_j means the converted mean value of COD_{cr} for the full tank by j measurements. Assuming the tank level is fixed, l, the sum of Eq. (6) in this case is an integral sum, therefore, its value does not really depend on the number of intervals (i.e., the number of measurements, n), only on the tank level, l.

The standard deviation is:

$$\Sigma_j^2 = \sum_{i=1}^{j} \sigma_i^2 \Delta l_i^2 \tag{7}$$

where $\sigma_i = \sigma(r_i^*)$. If $\Delta l_i \cong \Delta l = 1/n$, Eq. (7) can be transformed as follows using Eq. (5):

$$\Sigma_j^2 \cong \frac{1}{n}\sum_{i=1}^{j}\sigma_i^2 \Delta l_i = \Sigma_{l,n}^2 \quad (8)$$

where the sum is an integral sum too, so it does not depend on n either, therefore, the standard deviation square of cumulative COD_{cr} is inversely proportional to the number of measurements, n, i.e., it decreases with them. This is the basis of the model, since by introducing cumulative COD_{cr} the standard deviation can be significantly reduced. The upper value conforming to Eq. (4) for the cumulative COD_{cr} is:

$$K_{l,n}^+ = K_l + 1.64\Sigma_{l,n} \quad (9)$$

The following two additional limits can be defined, one is the limit of the converted mean value of COD_{cr} belonging to tank level l:

$$K_{l,\mathrm{LIMIT}} = l \cdot k_{\mathrm{LIMIT}} \quad (10)$$

The other is the value of $l = 1$, i.e., the maximum value of $K_{l,\mathrm{LIMIT}}$ (the permissible upper limit), which is:

$$K_{\mathrm{MAX}} = k_{\mathrm{LIMIT}} \quad (11)$$

This equals the threshold limit value of COD_{cr} in the full tank (Fig. 1).

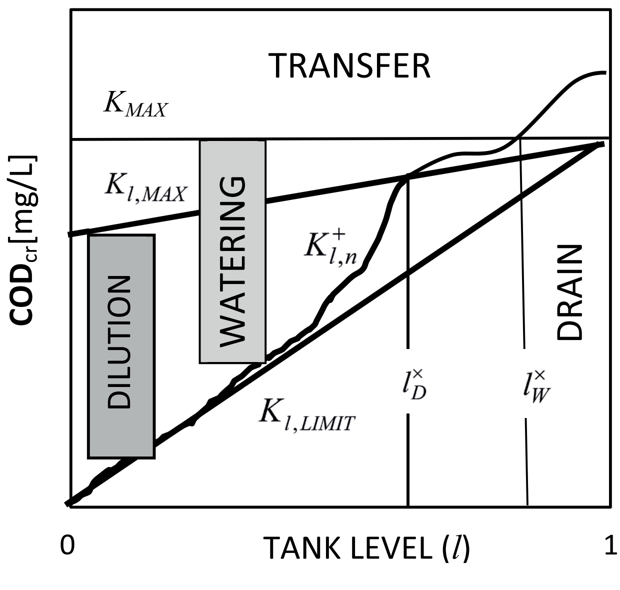

Fig. 1. Limit values of cumulative COD_{cr} as the function of the tank level, l, during watering treatment ($K_{l,\mathrm{LIMIT}}$, K_{MAX}) and the dilution treatment ($K_{l,\mathrm{LIMIT}}$, $K_{l,\mathrm{MAX}}$) with the upper limit ($K_{l,n}^+$) and the critical values of the tank level belonging to the dilutions ($l_W^\times$, $l_D^\times$).

3. Treatment technologies

The following possible technical solutions have been developed for the wastewater treatment. From a calculation perspective these can be arranged in two groups, watering and dilution by wastewater of low COD_{cr} content (Fig. 1). The diluter may be separated or treated by membrane filtration wastewater.

3.1. Watering treatment

The first technical solution is watering. This treatment decreases the COD_{cr} value under the limit by diluting wastewater with clean water.

For this treatment there are three possibilities: (1) if $K_{l,n}^+ < K_{l,\mathrm{LIMIT}}$, then the average COD_{cr} in the tank is less than the threshold k_{LIMIT} = 1,000 mg/L. In this case, the wastewater can be run into the drain at any time; (2) if $K_{l,n}^+ > K_{l,\mathrm{LIMIT}}$, but $K_{l,n}^+ < K_{\mathrm{MAX}}$, then the wastewater can be run out by watering; and (3) if $K_{l,n}^+ > K_{\mathrm{MAX}}$, it must be transferred (Fig. 1).

For the (critical) tank level $l_W^\times$, where it is decided that the wastewater is transported or run into the drain with watering, we have the following equation (Fig. 1):

$$K_{l=l_W^\times,n}^+ = K_{\mathrm{MAX}} \quad (12)$$

Watering is a theoretical possibility. Dilution with clean water is forbidden by regulations because the amount of total organic compounds into the drain does not decrease, which means neither does the environmental load. Generally, there are regulations on the total emission. The purpose of the watering description is to clarify the model, however, the calculation would be used for the dilution wastewater with a low COD_{cr} content from external sources.

3.2. Wastewater self-dilution treatment

If the previously mentioned dilution wastewater is not available from external sources, the second technical solution is to use wastewater with a low COD_{cr} content, which can be produced from own wastewater as well. Two tanks are needed for this, K to be diluted and D the diluter tank. The wastewater must be separated. Let us assume the COD_{cr} value for the separation is $k_{D,K}$ (200–300 mg/L), if the COD_{cr} value calculated from the measurement is:

- $k < k_{D,K}$, the wastewater is directed to the D tank (i_D) and
- $k > k_{D,K}$, the wastewater is directed to the K tank (i_K).

Let us assume a mean value of k_D and a standard deviation σ_D of COD_{cr} in the D diluter tank. In general, $k_D \leq k_{D,K}$ and $\sigma_D \to 0$ as tank D has been continuously filled up (and down) so $i_D \to \infty$.

The tank level limit $l_D^\times$ for the dilution, instead of Eq. (12), can be written as follows:

$$K_{l=l_D^\times,n}^+ + (1 - l_D^\times)k_D = K_{\mathrm{MAX}} \quad (13)$$

as the COD_{cr} of wastewater used for dilution has been added to the upper limit of Eq. (9), proportional to its volume. Using Eq. (13), the upper limit of Eq. (11) will now be:

$$K_{l,\mathrm{MAX}} = K_{\mathrm{MAX}} - (1-l)k_D \quad (14)$$

and linearly depends on l (Fig. 1). The value of k_D can be adequately estimated by $k_D \cong k_{D,K}$.

The whole treatment process can be seen in Fig. 2.

Both processes decrease the amount (and the cost) of wastewater transferred by lorry. At the same time, the load for the sewerage system increases, which can cause problems if the total COD_{cr} is limited. The next suggested treatment can decrease both, the lorry transfer part will be lower as it is a more concentrated solution on average.

3.3. Dilution treatment with membrane filtration

The dilution wastewater can partly be produced by membrane filtration. This is the third potential technical solution. Wastewater can be divided into two parts with membrane filtration, the first is a lower, and the second is a higher concentrated solution. A roughly threefold concentration difference can be obtained. If the wastewater has a COD_{cr} higher than a certain minimum value [12], the sucrose content can be fermented (in this case more than 10,000 mg/L is transferred free of charge, otherwise there is a considerable amount of transfer and processing charge). It is worth concentrating the wastewater with a membrane between a COD_{cr} of 3,000 and 10,000 mg/L. The fraction above 10,000 mg/L flows to a gathering tank (T) and is later transferred, the other fraction (COD_{cr} < 10,000 mg/L) flows to the K tank of Fig. 3.

4. Measurements

The main part of the dissolved or solubilised compounds of the water comes from washing the pharmaceutical instruments of the factory when changing manufactured medicines. This is a diluted coating solution for pills, and mainly contains sucrose as well as citric acid or its salts, surfactants and talcum powder. The base conductivity originates from the salinity of the water system.

The basic principle of our method is that the concentration of a sucrose solution can be measured by refractometrics, so we can expect a direct relation between the refraction (BRIX) value and the COD_{cr} value [13–19]. Since the refractometric measurement can be executed online, we assumed this measurement method would be the basis for this control system.

Numerous, in-service online measurements were carried out where the sucrose equivalent r (BRIX [%], 0–7), the conductivity Ω (0.7–33.6 mS/cm), the pH (5.9–8.5) and the temperature T (27°C–42°C) were determined. 120 samples were selected and for all samples the COD_{cr} was determined in a laboratory too (x_i). The samples can be regarded as independent [10,11].

To check the models, four virtual tanks, N^{r}1-4 (“drain”, “watering”, “transfer” according to the three treatment possibilities and “membrane” to membrane filtration) with 20 element samples (n = 20 and $\Delta l_i = \Delta l = 0.05$) were made from the data [11]. Using the correlations from Eqs. (2) to (3), the upper limit $K^+_{l,n}$ for the 95% probability was calculated from Eqs. (6) to (10) and displayed as a function of Eq. (5) tank level, and if l = 1 then $K^+_{l=1,n} = K^+_n$. Finally, the average COD_{cr} for the full tank was calculated, $K_{l=1} = K$, and compared with the determined values, $X = 0.05\sum_{i=1}^{20} x_i$ which, according to the model, equal the calculated and measured average COD_{cr} of the tank.

5. Results

Fig. 4 shows the three treatment possibilities of the virtual tanks (N^{r}1-3) according to Fig. 1: running to the drain (K^+_n = 410, K = 236, X = 247 mg/L), watering (K^+_n = 959,

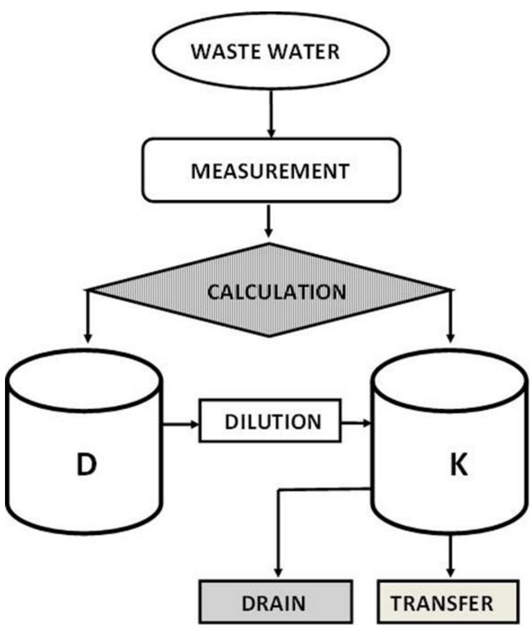

Fig. 2. Control system for wastewater self-dilution treatment.

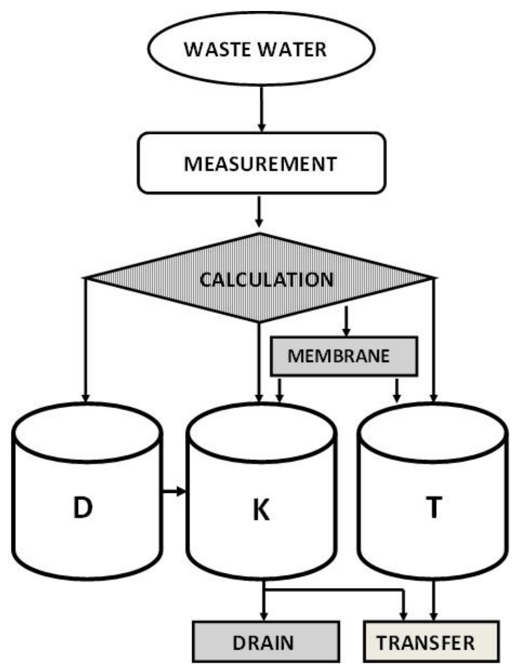

Fig. 3. Control system for the dilution model with membrane filtration.

K = 671, X = 728 mg/L) and transfer (K_n^+ = 2,943, K = 1,913, X = 2,234 mg/L).

In Fig. 5, two types of dilution and membrane treatment of the N^{r}4 virtual tank can be seen. In the case of dilution with water (watering) the tank level is $l_W^\times$ = 0.75, the water quantity needed for the dilution is $1 - l_W^\times$ = 0.25 tank, and K_n^+ = 998 mg/L, whilst the measured value before dilution is X = 718 mg/L. At watering the value of X equals to that after dilution.

For dilution with wastewater these values are: $l_D^\times$ = 0.6, $1 - l_D^\times$ = 0.4, K_n^+ = 911 mg/L and X = 625 mg/L. In the case of wastewater dilution, the COD$_{cr}$ value of wastewater into

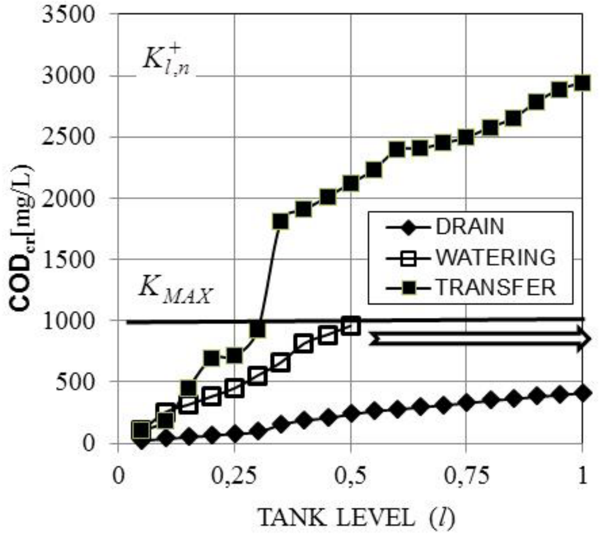

Fig. 4. Calculated data of COD$_{cr}$ upper limits, $K_{l,n}^+$ as a function of tank level, l at "drain", "watering" and "transfer" virtual tanks N^{r}1-3 with 20 elements for the three treatment possibilities (symbols) and the permissible upper limit K_{MAX}.

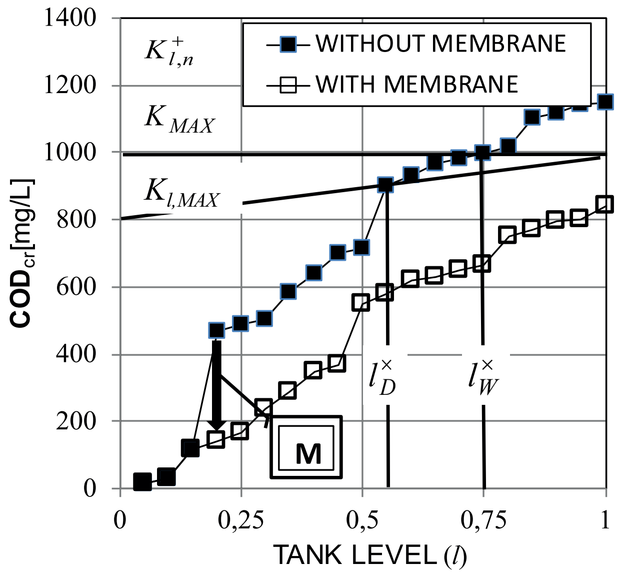

Fig. 5. Calculated data of COD$_{cr}$ upper limit, $K_{l,n}^+$ (symbols) with watering ($l_W^\times$) and dilution ($l_D^\times$) as a function of tank level l at the "membrane" virtual tank, with and without membrane.

the drain before dilution, X is generally lower as that at the watering, but freshwater is not necessary.

Using the membrane separation at sample 4 (k_4 = 7,000 mg/L), after the separation, a 0.05 wastewater volume (k = 21,000 mg/L) can flow into T tank. For this reason, the value of $K_{l,n}^+$ has decreased. As K_n^+ = 842 mg/L < 1,000 mg/L, the wastewater can run into the drain.

6. Discussion and summary

We have developed three possible treatment technologies to solve the discharge problem of wastewater with a high COD$_{cr}$ content. These were required because, without them, the COD$_{cr}$ content of the wastewater produced would exceed the threshold for discharge into the drain, and so has to be transferred (100% according to Fig. 5), or repeated penalties can be expected, generating additional cost.

The first technology dilutes with clean water; whilst this significantly reduces the volume transferred (to 25% in our case), and so the additional cost as well, diluting with clean water is acceptable neither legally nor from other perspectives. This technology would be applicable in the case of biologically cleaned communal wastewater with a low COD$_{cr}$ content (<50 mg/L).

The second option is diluting with own wastewater with a low COD$_{cr}$ content. This is less effective (volume to transfer 45%), but there are no obstacles to its use. Both technologies reduce the additional costs, but they do not reduce the COD$_{cr}$ value of the total wastewater (in fact, it could even rise owing to the smaller volume for transfer), so the environmental load could increase as well. There may also be provisions on the total discharged COD$_{cr}$ volume, which could limit its application.

Incorporating membrane separation into the technology can lower the additional costs more than the previous options (volume for transfer 5%, though this is free owing to the high COD$_{cr}$ content), but the total COD$_{cr}$ value of the discharged wastewater falls as well. Consequently, this latter version seems to be the most promising, but it must be considered that there are substantial investment costs involved. The model and the arrangements can be used in all cases when any key parameter (related to concentration) can be measured in real time with some online methodology.

The algorithm of the control module may be improved further [20,21] to reduce the cost further. In this area, the fuzzy control [22] could be effective, as was proven in a lot of similar cases. The optimal parameter values of the model were searched with genetic algorithms. The system can be kept optimal despite changes in technology, if the results of the control measurements are channelled back into this optimisation system [10]. Thus, the principle of our control system can be useful in different types of water solutions and in different industrial activities.

7. Conclusions

For the real-time definition of sucrose content in wastewater from a pharmaceutical factory, a complex system was developed. The system contains an online measuring module, which can mainly measure the BRIX and conductivity values of the water. Furthermore, a real-time control module was developed, which endeavours to adjust the parameters of the wastewater to keep it continuously under the threshold value. It works with three collecting tanks, controls the flow of the water into the tanks, and afterwards, releases the water into the drain or suggests transfer for COD_{cr} removal. The equipment was tested for 45 d, and the measured data were used for simulated tests of the control module.

The results show that if the simulated control system is used, the costly truck shipping transfer to remove COD_{cr} from the system decreases by 50% while in the same time no water above the threshold value would flow into the sewerage system. The main advantage of the developed concept and model is that it can treat wastewater streams with a fluctuating flow rate and with rapidly changing quality (COD_{cr}) through processing online data provided by simplified measuring methods in a real-time manner. This way, a reliable and easily adjustable quality of wastewater can be fulfilled for discharge to the recipient in the case of a parameter such as COD_{cr}.

The introduced treatment methods, watering (external wastewater with low COD_{cr} content), self-dilution and membrane technology were introduced to show alternatives for the technical treatment possibilities upon the results of the model. Using this or similar models are very useful in most cases when the measurement of a certain parameter or parameters is not possible or not practical, or takes too much time. The results open up new dimensions of wastewater technology.

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Symbols

K	—	Mean value of cumulative COD_{cr}, mg/L, L
R^2	—	Correlation coefficient
T	—	Temperature, °C
Σ	—	Standard deviation of cumulative COD_{cr}, mg/L
Ω	—	Conductivity, mS/cm
X	—	Measured value of cumulative COD_{cr} before dilution, mg/L
k	—	Mean value of COD_{cr}, mg/L
l	—	Tank level
n	—	Number of measurements
r	—	Refraction, BRIX [%]
t	—	Time (min)
x	—	Measured value of COD_{cr}, mg/L
κ	—	Random variable of COD_{cr}, mg/L
σ	—	Standard deviation of COD_{cr}, mg/L

Superscript

x	—	Critical value
*	—	Corrected value
+	—	Upper value

Subscript

D	—	Diluted, diluter tank
i, j	—	Series number of measurements
K	—	Diluted tank
l	—	Tank level
LIMIT	—	Upper limit for l tank level
MAX	—	Upper limit for full tank
W	—	Watering

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