Abstract
This paper refers to the study of the efficiency of the constructed wetlands in the wastewater treatment, via mathematical modeling. The propose is to determine the stabilization limit value of removal of some parameters: Chemical Oxygen Demand (COD), Ammoniacal Nitrogen and Conductivity. The research considered a constructed wetland system, in an experimental scale, with different hydraulic retention time (HRT) for domestic wastewater treatment: 0, 2, 4, 6 and 8 days. The data were collected, analyzed and the results indicated, according to the Ford-Walford method, the removal stabilization limit values were, approximately, 90% for COD, 74% for Ammoniacal Nitrogen and 41% for Conductivity. According to the model, the hydraulic retention time to reach these removal indexes were 4 days for Ammoniacal Nitrogen and Conductivity and 10 days for COD. The evaluated parameters have demonstrated to be sensitive to the biological wastewater treatments by constructed wetland, the model made it possible to determine the limit values and the stabilization time and the hydraulic retention time has showed an important factor of the management of such systems, that must be monitored, in order to optimize the parameters removal and the efficiency of the treatment.

Keywords: efficiency of a constructed wetland, hydraulic retention time, stabilization limit value.
Introduction
The society development as a whole has led to an increase in water consumption and, as a result, increasing volumes of sanitary sewage that require adequate treatment and disposal to avoid pollution problems and contamination of the environment, with consequent serious health risks to the population. Even today, the part of the population that is not served by wastewater collection and treatment systems, or assisted by sub-efficient systems, reinforces the need to study, develop and apply viable technologies of decentralized treatments that may favor regions distant from urban centers or with limited supply of public services (Elzien et al., 2016).

Thus, constructed wetlands become a viable and efficient sewage treatment technology whose implementation is characterized by low cost and ease of operation, including a pleasant visual appearance due to the vegetation that composes the system ((Mello et al., 2019; Dou et al., 2017; Ilyas and Manish, 2017; Gikas and Tsihrintzis, 2014; Saeed and Sun, 2015; Chang et al., 2012).

Constructed wetlands can be used in both wastewater treatment and post-treatment, in several ways, and they can work in accordance with the flow regime: vertical, horizontal, superficial or subsurface horizontal (Vyzamal, 2008). These beds are composed of macrophytes plants and substrates (Sabokrouhiyeh et al., 2016; Calheiros et al., 2009). The substrates constitute a filter media for the waste and support for the roots of plants which, together with microorganisms, favor the removal of nutrients through various biological processes, promoting the wastewater treatment (Adera et al., 2018; Matos et al., 2018; Ebrahimi et al., 2013).

Regarding the post-treatment of domestic effluents, using constructed wetland systems, the hydraulic retention time (HRT) is an important factor because, according to the literature, the parameters removal efficiency can be reduced due to the appearance of limiting conditions as the low hydraulic retention time (Matos et al., 2018; Chang et al., 2012). The influence of HRT removing of organic load and nutrients has been studied in order to optimize and guarantee a better quality of the final effluent (Otieno et al., 2017; Upadhyay et al., 2016; Munoz et al., 2016; Ewemoje et al., 2015).

The hydraulic retention time is related to the average time the effluent remains in the system and the efficiency in the parameters treatment improves as the retention time of the effluent increases Sehar et al., 2015; Lee et al., 2014) and mathematical models of prediction can help in the management of the systems, determining the hydraulic retention time that allows greater removal, as well as indicating the maximum removal possible in a given system. Considering the parameters: chemical oxygen demand (COD), Ammoniacal nitrogen (AN) and conductivity (C), the objective of this research was to analyze the stabilization limit value of their removals, through the mathematical modelling, and to determine the appropriate HRT for the guarantee of treatment efficiency (Szypula et al., 1987).
The parameters were selected because their reduction is of extreme relevance to improve the quality of the wastewater and, consequently, to reduce impacts on the environment arising from the releases of these effluents. The COD measures the amount of organic matter susceptible to being oxidized by chemical means; it refers an important study factor of wastewater that evaluates the amount of oxygen dissolved in acid medium that leads to the degradation of matter. Concerning ammoniacal nitrogen, it is related to the decomposition of matter and to the transformations suffered by the organic compounds present in the sewage and the conductivity is linked to the salts and chlorides that are not removed in the conventional wastewater treatments (Ramprasad et al., 2017; Bumgarnera et al., 2007).

Materials and methods

Experimental setup
The system used in this study was constituted of anaerobic wastewater reactor UASB, Up flow Anaerobic Sludge Bed, in a batch regime, with retention time adjustments and it was connected in a constructed wetland that has operated in subsurface horizontal flow and worked as a post-treatment of domestic sewage, Figure 1:

![Figure 1. System used constituted by UASB reactor and horizontal flow wetland.](image-url)

Collections and Analysis
In order to evaluate the wetland performance in post-treatment of sanitary sewage, the experiments were performed in triplicate considering 0, 2, 4, 6 and 8 days of hydraulic retention. The analyzes followed the procedures according to (APHA, 2012).
The methods used in the analyzes were in accordance with Standard Methods for the Examination of Water and Wastewater: SMEWW (22nd ed) Method 5220 D, 4500-NH3 C and 2510 B for COD, ammoniacal nitrogen and conductivity, respectively (APHA, 2012). The temperature (°C) e pH were also monitored according to Method 2550 B and 4500 B, respectively.

Considering the upward behavior of the removal of parameters, at the beginning of treatment, and its stabilization, after a period of operation, it is possible to analyze this stabilization limit, as well as the time needed to obtain this limit and improve de efficiency of the system.

So, for the study of this stabilization limit for removing parameters and determination of the time necessary for such reach, based on the assumption that the parameters removal in wetlands increase (Midhun et al., 2016) according to the HRT and tend to stabilize after a certain time, the Ford-Walford method was applied (Szypula et al., 1987).

This method is based on the asymptotic behavior of the phenomenon and allows to determine the stabilization value of the system (Szypula et al., 1987).

Considering the removal values (of COD, ammoniacal nitrogen and conductivity) given generally by \((R_t, R_{t+1})\), with \(R_t = R(t), t \in [0, T]\), the adjustment seeks to establish a continuous function \(g\) where \(R_{t+1} = g(R_t)\).

Thus, assuming \(R_t \approx R_{t+1}\), the stabilization value (percentage), \(R^*\), is a fixed point of the function \(g\) of the form: \(R^* = g(R^*)\).

In fact, because:

\[
R^* = \lim_{t \to \infty} R_{t+1} = \lim_{t \to \infty} g(R_t) = g \left( \lim_{t \to \infty} R_{t+1} \right) = g(R^*)
\]

Therefore, according to the method, the stabilized value of the removal \(R^*\) is determined by finding the adjustment function \(g\), solving Equation (1):

\[
\begin{align*}
&\{R_{t+1} = g(R_t) \\
&R_{t+1} = R_t
\end{align*}
\]

Equation (1)

Obtained \(R^*\) for the parameters, it were determined the asymptotic exponential curves \(R = R(t) = R^* - Ae^{Bt}, R^* > 0, B < 0, t\) the hydraulic retention time (HRT) and \(R_t\) the percentage of the respective COD, ammoniacal nitrogen and conductivity removals.
Results and discussion

Samples collected were analyzed and the values obtained for Chemical oxygen demand (COD) (mg/L), ammoniacal nitrogen (AN) (mg/L) and conductivity (C) (uS/cm), considering 0, 2, 4, 6 and 8 days of hydraulic retention time (HRT), are presented in Table 1.

Table 1. Average values and standard deviation of Chemical oxygen demand (COD), ammoniacal nitrogen (AN) and conductivity (C) values obtained at the beginning of the system’s operation (0) and with 2, 4, 6 and 8 days of hydraulic retention time (HRT).

| HRT (days) | COD (mg/L)  | AN (mg/L) | C (uS/cm) |
|-----------|-------------|-----------|-----------|
| 0         | 82.10 ± 0.00| 31.38 ± 0.00| 470.00 ± 0.00|
| 2         | 51.10 ± 2.95| 9.25 ± 1.96 | 282.70 ± 23.46|
| 4         | 22.20 ± 0.43| 7.85 ± 1.39 | 282.40 ± 15.54|
| 6         | 14.30 ± 0.35| 7.85 ± 0.42 | 266.20 ± 16.36|
| 8         | 16.20 ± 1.55| 8.96 ± 0.46 | 277.50 ± 19.70|

The system, in uncontrolled environment, worked at an average ± standard deviation temperature of 23.44 ± 0.99 °C and pH of 5.86 ± 0.09 indicating an acidic effluent.

The biological processes that occur in constructed wetlands contribute to removal of nutrients and, consequently, to the treatment of sewage. Besides that, the pH and temperature are among the main parameters that influence the removal of organic matter and nitrogen in biological wastewater treatments (Saeed and Sun, 2012; Sultana et al., 2015).

This fact occurs because the microorganisms in these systems are affected by these parameters. Propitious environments alter the dynamics of microorganism populations, which corroborates the removal of organic matter. According Ji et al. (2020) low temperatures can affect the performance of plants and microorganisms in removing organic matter and nutrients. This parameter that can be related to the efficiency of wetlands, low temperatures can affect the performance of plants and microorganisms in removing organic matter and nutrients, such as phosphorus and total nitrogen, in addition to ammonia nitrogen. He et al. (2012) claim that there is a positive correlation between higher temperatures and removal of ammoniacal nitrogen.

According to analyze, the percentage of removal (%) of COD, ammoniacal nitrogen (AN) and conductivity (C), considering 0, 2, 4, 6 and 8 days of hydraulic retention (HRT), are presented in Table 2.
Table 2. Percentage of removal, in terms of the HRT, of Chemical oxygen demand (COD), ammoniacal nitrogen (AN) and conductivity (C).

| HRT (days) | COD (%) | AN (%) | C (%) |
|------------|---------|--------|-------|
| 0          | -       | -      | -     |
| 2          | 37.8    | 70.5   | 39.8  |
| 4          | 73.0    | 75.0   | 39.9  |
| 6          | 82.6    | 75.0   | 43.4  |
| 8          | 80.2    | 71.4   | 40.9  |

The monitoring of the hydraulic retention time of the system is important when the objective is to obtain maximum treatment efficiency. Silva et al. (2020) tested the influence of hydraulic retention time on the removal of parameters such COD and total nitrogen considering aeration factors in the operation of the wetlands. Merino-Solis et al. (2015) made tests assessing this influence on nutrients removal considering constructed wetlands and anaerobic filters.

The efficiency of a system is closely related to the infrastructure, resources, type of operation, as well as characteristics of effluent to be treated and parameter to be removed. In this way, the performance of a constructed wetlands must be evaluated to obtain the best treatment, considering its characteristics and operating conditions.

The initial COD at the wetland was 82.10mg/L. In 2 days of HRT this value reduced to 51.10mg/L (37.8% removal). In 4 days of HRT the value reduced to 22.20mg/L (73.0% removal). In 6 days, it reduced to 14.30mg/L (82.6% removal) and in 8 days of HRT the value of COD increased to 16.20 mg/L (approximately 3% increase over the first six days of HRT). The removal of COD is an important indicator for assessing the efficiency of the treatment system. Regarding the model, by setting the relation \( R_t, R_{t+1} \), and assuming its convergence to \( (R^*, R^*) \), the stabilized removal percentage was: \( R^* = 89.9\% \) for COD, Figure 2.

For ammoniacal nitrogen, it was verified 31.38mg/L in the entrance of the system. In 2 days of HRT this value reduced to 9.25mg/L (70.5% removal). In 4 days of HRT the value reduced to 7.85mg/L from 4 (75.0% removal). In 6 days, this value was maintained and in 8 days of HRT the value of ammoniacal nitrogen increased to 8.96mg/L (approximately 5% increase over the first six days of HRT). Ammoniacal nitrogen causes toxicity to aquatic organisms, so its removal before the effluent is released into the water system is of fundamental importance. About the stabilized removal percentage for ammoniacal nitrogen was \( R^* = 73.8\% \), Figure 3.
Figure 2. Experimental and foreseen COD removal (%) for different HRT’s.

Figure 3. Experimental and foreseen ammoniacal nitrogen removal (%) for different HRT’s.
For conductivity, 470.00uS/cm was initially found. This value was reduced to 282.70uS/cm in 2 days of HRT (39.8% removal). In 4 days of HRT the value was 282.40uS/cm (39.9% removal). In 6 days, the reduction was 266.20uS/cm (43.4% removal) and in 8 days of HRT the value of conductivity increased to 277.50uS/cm (approximately 5% increase over the first six days of HRT). The conductivity presented a stabilized removal percentage of $R^* = 41.4\%$, Figure 4.

Figure 4. Experimental and foreseen conductivity removal (%) for different HRT's.

In general, the data indicated COD, ammoniacal nitrogen and conductivity removal efficiency. The removal percentage of the parameters was gradual in the first six days of HRT, showing more pronounced in the first four days and, although still increasing, less pronounced in the sixth day of HRT.

From the sixth day, the system showed signs of saturation. It was observed an increase in COD, ammoniacal nitrogen and conductivity present in the effluent samples, which may be related to the gradual loss of water from the system, which made it difficult to collect samples after the eighth day.

The adjusted asymptotic exponential removal curves for COD, AN and C were:

\[
R(t)_{\text{COD}} = 89.93 - 89.93 \times \exp(-0.272t)
\]
\[
R(t)_{\text{AN}} = 73.79 - 73.79 \times \exp(-1.66t)
\]
\[
R(t)_C = 41.1 - 41.4 \times \exp(-1.64t), \text{ respectively.}
\]
According to the model, the removal stabilization percentage achieved with 4 days of HRT for ammoniacal nitrogen and conductivity and with 10 days for COD.

The COD and ammoniacal nitrogen removal have great influence on hydraulic retention time: the higher the HRT, the greater the removal of these parameters (Ramprasad et al., 2017). Studies by Mello et al. (2019), with comparison of different HRT's, showed removals that reached 82% with HRT of 48 hours for COD and 47% in 72 hours of HRT for Nitrogen (Sultana et al., 2016) achieved COD removal of 96.84% in 8 days of retention.

For ammoniacal nitrogen and organic matter, (Cui et al., 2015) evaluated 1, 2 and 3-day retention times in different wetlands configurations and obtained better removals in 2-day time for both parameters. In the research conducted by Merino-Solís et al. (2015) 3 different HRT's were considered (2, 3 and 4 days) in subsurface flow wetlands, reaching 81.7% COD removal with 4 days of hydraulic retention.

For total nitrogen, (Merino-Solís et al., 2015) found better removal of 40% with HRT of 4 days. In a study by Munõz et al. (2016), the results for COD and ammoniacal nitrogen removal were 69.1 and 44%, respectively, for 7 days of HRT.

In the comparison of the COD and ammoniacal nitrogen removal, in the 4-day retention times, the values obtained by (Zhang et al., 2012) were 98.5% for COD and 95.2% for ammoniacal nitrogen.

In a study by (Upadhyay et al., 2016), ammoniacal nitrogen and conductivity removal for 2 days of HRT reached 50.48% and 21.56%, respectively.

For the nutrient’s removal, several authors indicate 10 days of HRT. The recommended HRT in wetlands projects varies from 10 to 13 days (Merino-Solis et al., 2015). According to Zhang et al. (2012), the most effective times for parameters removal are between 4 and 15 days.

Specifically, for subsurface flow wetlands, Wu et al. (2015), recommend from 2 to 5 days of hydraulic retention.

Evaluating the results of the experiments, the presented system proved to be efficient in the parameters removal, corroborating with the literature that the HRT is directly related to the efficiency of parameters removal. It should be noted that the parameters removal percentages analyzed were relatively high and, in some cases, higher than the values found in literature.
Conclusions
The constructed wetland system presented good removal efficiency as a post-treatment wastewater for domestic use. The system was operated with different HRT's and had as objective to evaluate the percentage removal limit of the parameters.

The study demonstrated that the removal efficiency of certain compounds depends on the hydraulic retention time applied in the operation of the operated systems, since the parameters removal is limited by the residence time of the system affluent.

The hydraulic retention time to reach the stabilized removal percentage of approximately 90% for COD was 10 days. For nitrogen, it was found that the stabilized removal percentage at 74% was reached in 4 days, time also appropriated to reach a percentage of 41% of conductivity.

The stabilization removal values (percentages) obtained with the model appliance were reached experimentally and could be compared with the existing literature.

The implanted system indicated relatively optimized hydraulic retention times to reach the stabilized removal of the parameters, considering the recommended time in wetlands projects ranging from 10 to 13 days of HRT.

The open-air system was subject to bad weather conditions and presented water loss through evaporation. This factor made collection and analysis impossible with higher HRTs.

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