



Water temperature effect on the reaction rate constant of pollutants in a constructed wetland for the treatment of swine wastewater



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Abstract:

Temperature is an important factor in the processes that are carried out in biological systems. In wetlands, the capacity to remove pollutants is limited by environmental factors. The objective was to determine the effect of water temperature on the rate constant for the removal of pollutants in wastewater from pig farms. The evaluation was carried out in a surface flow constructed wetland (SFCW) consisted of a 9 m long and 3 m wide channel covered with a high density geo-membrane (4 mm). The SFCW bed consisted of a 30 cm layer of sand and clay; native vegetation from the study area was used. The hydraulic

retention time (HRT) was 10 d, and 12 experimental runs were carried out between January 2014 and December 2015. The results showed an average removal rate of the chemical oxygen demand (COD) of approximately 75 and 74 % for 2014 and 2015 respectively; the average removal rate of ammonia nitrogen (NH₃-N) of 65 and 69 %, while the average total nitrogen (TN) removal rate was 69 and 63 % and the total phosphorus (TP) removal rate was 75 and 73 % in 2014 and 2015, respectively. The water temperature along the experimental phase ranged from 13 to 22 °C. The removal of NH₃-N showed the highest dependence on water temperature with values of $R^2 = 0.8787$ in 2014 and $R^2 = 0.8957$ in 2015. The volumetric reaction constant ($k_v \text{ d}^{-1}$) in 2014 ranged from 0.041 to 0.185 d^{-1} with an average temperature in the wetland of 13 to 21 °C. While k presented an average value of 2.60 cm d^{-1} in 2014, and in 2015 the observed value was 3.22 cm d^{-1} . It was evident that the value of k_v augmented as the water temperature increased, which indicates that this factor has a direct effect on the removal of the NH₃-N.

Key words: Temperature, Reaction rate constant, Wetlands, Swine wastewater.

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Introduction

In Mexico, the increase in the discharge of wastewater from various activities has caused certain receptor bodies of water to exhibit different types and levels of pollution, generating a strong impact on the reduction of this resource which, unless treated with viable alternatives for its recovery, may cause irreversible damage⁽¹⁾.

Approximately 420 m^3 of wastewater are generated every second in Mexico; of these, 250 $\text{m}^3 \text{ s}^{-1}$ are municipal, and 170 $\text{m}^3 \text{ s}^{-1}$ are non-municipal; less than 25 % of the latter, the most polluting of which are issued by pig farms, receive no treatment⁽²⁾. For this reason, special attention has been given to the use of effective, environment-friendly technologies to remove the pollutants present in waste water, especially the nutrients such as nitrogen and phosphorus^(3,4). Conventional wastewater treatment technologies are generally effective. However, many of these technologies involve high installation costs and use large amounts of energy.

Certain researchers have proposed the use of constructed wetlands (CWs) as a viable alternative for removing nutrients from livestock wastewater^(5,6). The processes carried out in these systems are sundry, but the main nutrient removal processes are the growth of the microbial biomass and the adsorption of the nutrients by the vegetation^(5,7). The efficiency of the CWs in the removal of pollutants has been widely researched by several authors⁽⁸⁻¹¹⁾. Constructed wetland can reach levels of ammonium removal of 80 to 99 %^(12,13,14).

The most important factors to be considered in the design of a wetland for its proper operation are the inflow, the load of organic matter, and the hydraulic retention time (HRT)^(15,16,17), although temperature is the primordial factor, as biological systems are involved^(18,19,20).

According to certain authors⁽⁶⁾, the efficiency of the wetland is segmented into seasonal cycles, and the effect of the temperature on the biotic reactions is greater at low temperatures (>15 °C) than at high temperatures (<20 °C). However, if the inflow and the concentrations in the wetland also vary seasonally, their affect will blend together with that of temperature⁽²¹⁾. The temperature also influences the denitrification process in the wetlands, which occurs under conditions of anoxia in the sediment or in anoxic micro-sites in the film adhered to the substrate or the tissue of plants⁽²¹⁾. Through this mechanism, nitrates can be removed in the wetlands^(22,23). In shallow wetlands, the process or degree of denitrification can reportedly be increased, due to the proximity of the nutrients in the sediment-water component⁽²⁴⁾. For this reason, denitrification has been regarded as a very viable method for removing nitrogen from the wetlands⁽²³⁾.

In a study carried out in Tennessee, USA, to assess the effect of vegetation and the HRT on pollutant removal capacity in wetlands, the average removal rate was found to be higher when using 6 days of HRT, compared to 2 days. Wetlands with vegetation exhibited favorable results; with 6 days of HRT, removal averages of 67 % were reported for the removal of ammonia nitrogen (NH₃-N), and values ranging between 42 and 67%, for the chemical oxygen demand (COD); synthetic wastewater was utilized to simulate agricultural runoffs⁽²⁵⁾. The capacity to remove total nitrogen (TN), NH₃-N, total phosphorous (TP) and COD using a sub-surface wetland in domestic wastewater was assessed in Hong Kong. Two WRTs (5-10 days) and wetlands with and without vegetation were used. The results showed greater removal in wetlands with vegetation using the two retention times. A 68 and 72 % COD removal rate was obtained in wetlands with vegetation; the removal rates were 92 and 95 % for NH₃-N, 65 and 62 % for TN, and 67 and 52 % for TP for days 10 and 5, respectively. The quality of the water obtained in the effluent met the standards of Hong Kong for use in recreational parks⁽²⁶⁾. Another author⁽²⁷⁾ researched the factors that affect phosphorus retention in a surface flow constructed wetland using wastewater from surface runoffs. The research was performed under cold environmental conditions in Norway. The results showed an average 21 to 44 % reduction of phosphorus. However, the removal percentage was observed to increase with a greater hydraulic load; the statistic results showed that the removal was influenced by different variables, such as the concentration of phosphorus in

the influent, the time of the year, the phosphorus content of the suspended solids, and the sedimentation rate of phosphorus.

Constructed wetlands have also been utilized to treat wastewater from pig farms. In southern China, 2 SFWs were established using *Vetiveria zizanioides* in one, and *Cyperus alternifolius* in the other. The objective was to research the efficiency of the wetlands in the removal of organic matter from the wastewater from pig farms through the seasonal changes during four years. The removal of COD and the biological oxygen demand (BOD₅) was 70 and 80 % in the spring, using two days of HRT. The removal rate was also reported to have reached up to 90 % in the summer, and to have dropped to 50 % for COD and 60 % for BOD₅ in the fall. No significant differences were found between the two wetlands under experimentation; however, the difference between seasons of the year was significant⁽²⁸⁾.

The availability and quality of water is a primordial need. However, there are risk factors associated to human activities and environmental factors, such as climate change⁽²⁹⁻³²⁾. The effects of extreme climate events are predicted to be reflected at once, primarily in food safety, as well as the availability of water for the various human activities^(29,32,33). The efforts to preserve this resource involve the use of alternative treatments that have a low installation cost and are environment friendly. Studies on the effect of the operational factors on the efficiency of the SFCW are numerous and sundry. However, so far, information about the SFC's pollutants removal efficiency related with the water temperature is scarce. The objective of this study was to determine the reaction rate constant of NH₃-N, as well as to identify the seasonal effect of the water temperature on the removal rate of the COD, NH₃-N, TN and TP contained in wastewater from pig farms through the use of a surface flow constructed wetland at pilot scale, in an effort to determine the functionality of this system under the climate conditions of the Highlands of Jalisco.

Material and methods

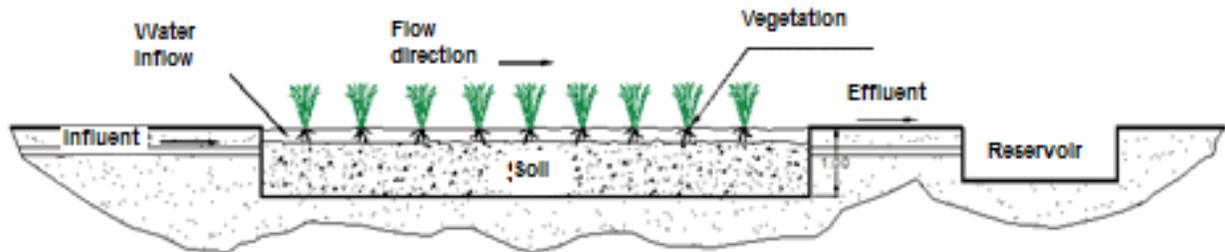
Characteristics of the farm

The research was carried out at the Santa María farm, located in the municipality of Arandas, in the state of Jalisco, 11 km to the northeast of the city of Arandas. The pig farm has 12 stalls, housing a total population of 12,000 pigs with some variations. For the intake process by the pigs and the cleaning of the pig pens, an average of 120,000 L d⁻¹ of potable water are used and subsequently piped into a biodigester for decomposition of the organic matter; the effluent of the biodigester is then routed to a sedimentation lagoon.

Design of the system

The variables considered in its design and construction were substrate, vegetation and water retention time. The surface flow wetland was built as a 9 m long x 3 m wide canal (Figure 1), with a 30 cm thick layer of a mixture of yellow sand and *tezontle* (volcanic rock) as support material for the vegetation and an approximately 5 % slope. The wetland was built with a (4 mm thick) high-density polyethylene geo-membrane, metal poles and a mesh as support for the channel. Vegetation (*Thypha sp.* and *Scirpus sp.*) from the surroundings of the farm was transplanted into the system and was maintained for a period of two months until it adapted to its new substrate.

Figure 1. Design of the surface flow wetland



Operation of the system

The wastewater used in his research was taken from the sedimentation lagoon at the outlet of the anaerobic digester. Because the concentration of the organic matter in the lagoon was approximately $7,160 \text{ mg L}^{-1}$ of COD, it was necessary to dilute it with well water in order to obtain the desired concentration for the research. The water from the lagoon and from the well was pumped into a 2,500 L storage cistern equipped with fluxometers for regulating the amount of water required by each influent and thus obtaining the desired COD concentration. The cistern had an electric mixing motor connected to a pair of blades that were kept in constant motion.

Experimental design

The organic matter content and the temperature of the water were regarded as independent variables. The dependent variables were: the COD, NH₃-N, TN and TP. Twelve experimental runs were carried out with a water retention time of 10 days and an organic load of 835 ± 64 mg L⁻¹ of COD in 2014 and 774 ± 26 mg L⁻¹ of COD in 2015.

Sampling and simple analysis

Samples were collected at the inlet and outlet the wetland, at 5-day intervals, and, on a weekly basis, from the sedimentation lagoon. The measured parameters were: Temperature (°C) (NMX-AA-007-SCFI-2000), COD (HACH 800 Method), TN (HACH 10072 Method), NH₃-N (HACH 10031 Method) y TP (HACH 10127 Method). The equipment used consisted of a HATCH DRB 200 reactor and a HACH DR 2800 spectrophotometer.

Statistical analysis

An ANOVA was performed in order to determine the significant differences between the two years of the study period at a 0.05 confidence interval.

Estimation of the reaction rate constant and the temperature coefficient for NH₃-N

The biological reactions occurring in the wetlands are generally described as first-order reactions. The first-order models usually work well in the long term⁽²¹⁾. In this study, the monthly averages of the concentrations of the constituents were determined for the assessment of the reaction rates.

The following first-order equation for a piston flow was utilized to describe the removal rate of NH₃-N:

$$\frac{C_e}{C_0} = \exp\left(\frac{-kv}{HRT}\right) \quad \text{eq. 1}$$

Where:

C_e is the average $\text{NH}_3\text{-N}$ concentration in the effluent (mg L^{-1});

C_0 is the average concentration of the nutrient in the influent (mg L^{-1}), and

k_v is the volumetric removal rate constant (d^{-1}).

The values of k_v were estimated using the following equation:

$$k_v = \frac{-\ln\left(\frac{C_e}{C_0}\right)}{HRT} \quad \text{eq. 2}$$

According to others authors⁽³⁰⁾, the areal removal rate constant is expressed as follows:

$$k = k_v * \varepsilon * h \quad \text{eq. 3}$$

Where:

k is the temperature dependent removal rate constant in a given area (cm d^{-1});

ε is the porosity constant of the fraction of space through which water can flow in the wetland (and which has been estimated for the several types of wetlands: 0.75 for the surface flow wetland, and 0.4 for the sub-surface flow wetlands);

h is the depth of the system^(21,34).

Equation 1 can be modified substituting k_v by using equation 2, as follows:

$$\frac{C_e}{C_0} = \exp\left(\frac{-k}{HLR}\right) \quad \text{eq. 4}$$

Where:

HLR is the hydraulic load (cm d^{-1}).

The effect of temperature on k_v or k can be summarized using the Arrhenius equation:

$$k_v = k_{v20} * \theta^{(T-20)} \quad \text{eq. 5}$$

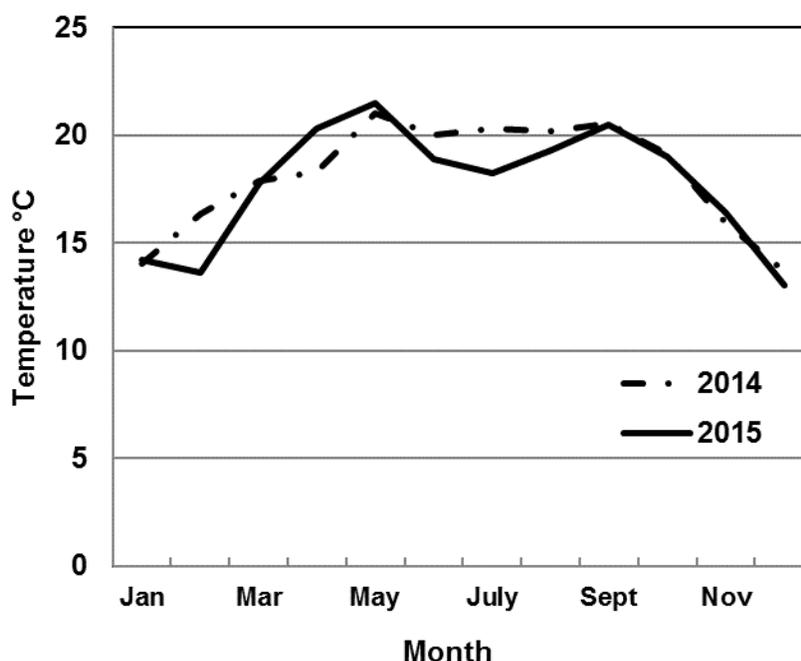
Where;

K_{v20} is the volumetric removal constant at 20 °C (d^{-1}); θ is the temperature coefficient, and T is the temperature of the water (°C). The slope $\ln(\theta)$ and the intersection of the line $\ln(k_v)$ were estimated by charting $\ln(k_v)$ vs $(T-20)$ and through a linear regression analysis. The coefficient of determination (R^2) was estimated in order to assess the adjustment of all the regressions.

Results and discussion

The average temperature of the water in the influent of the wetland in the year 2014 was 18.1 ± 2.2 °C, while in 2015 the average temperature was 17.7 ± 2.6 °C. Figure 2 shows the behavior of the monthly average of the temperature. In 2014, the lowest temperature (°C) was observed in December (13.6 °C), while the highest occurred in May (21 °C). The same behavior was observed in 2015, with the lowest temperature occurring in December, with an average value of 13 °C, and the highest temperature was observed in May (21.5 °C). In the year 2014 there was a stage during which the variability remained without significant changes (June – September), and then the temperature descended gradually until reaching the minimum level in the month of December. It may also be observed that the changes in temperature were more drastic in 2015 during the same months (June – September), reaching a minimum in December. Therefore, it is important to consider the seasonality, with the consequent influence of the rainy season on the low temperature of the water –a condition to be expected.

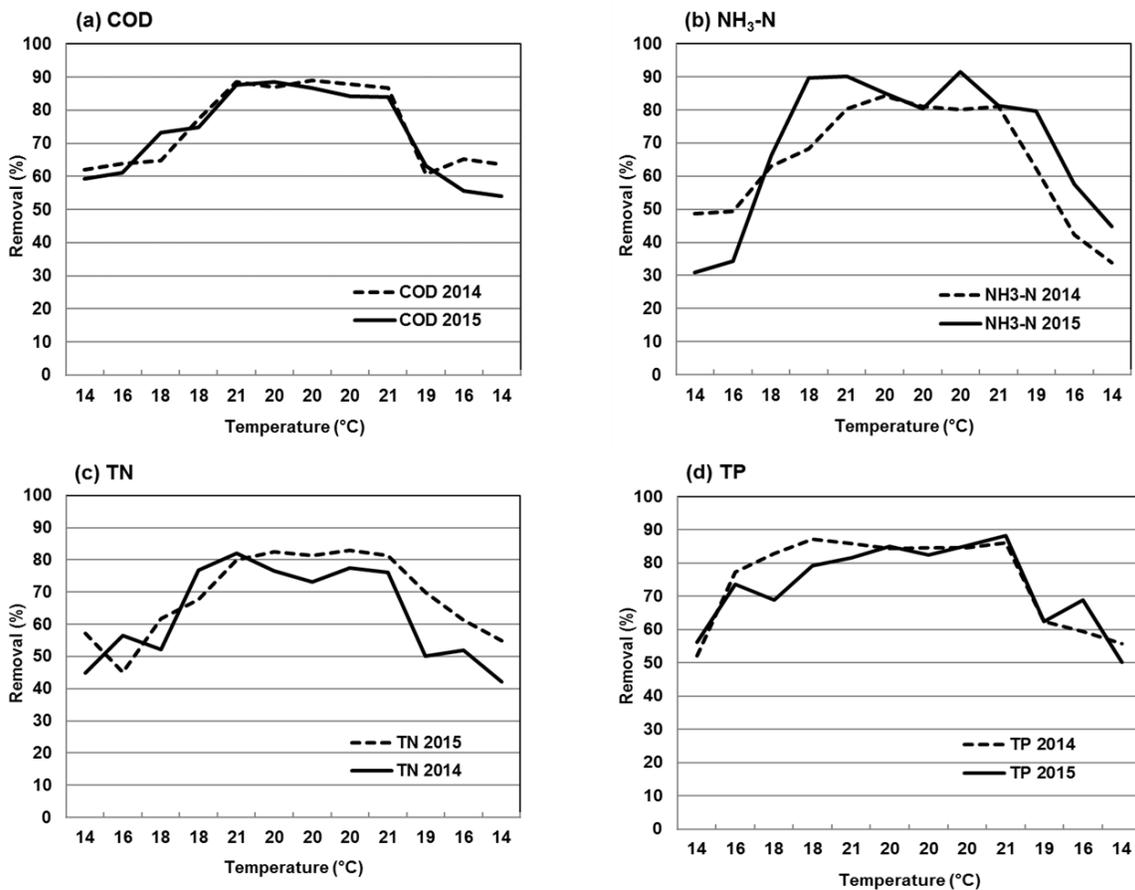
Figure 2: Monthly average temperature at the influent of the wetland in 2014 and 2015



The results of the efficiency of the SFCW for the removal of the organic matter are shown in Figure 3a. As may be observed, the average removal rate of COD in the year 2014 was 75 ± 12 %, while in 2015 the average was slightly lower, with a value of 74 ± 13 %. The minimum removal rate in 2014 (37 %) occurred in January, with an average temperature of the water

of 14 °C, and the maximum removal rate (76 %) was reached in May, with an average temperature of the water of 21 °C. The minimum removal rate in 2015 (54 %) occurred in December, when the average temperature of the water was 13 °C. The maximum value (89 %) was obtained in June, when the average temperature was 19 °C. The removal rate of COD was stable during the years of study. Notably, for instance, in winter the removal rate was approximately 60 %, increasing by approximately 10 % in spring; the system may be observed to have attained its maximum capacity in the summer, with a COD removal rate of approximately 88 %, while in the fall, it ranged between 60 and 70 %.

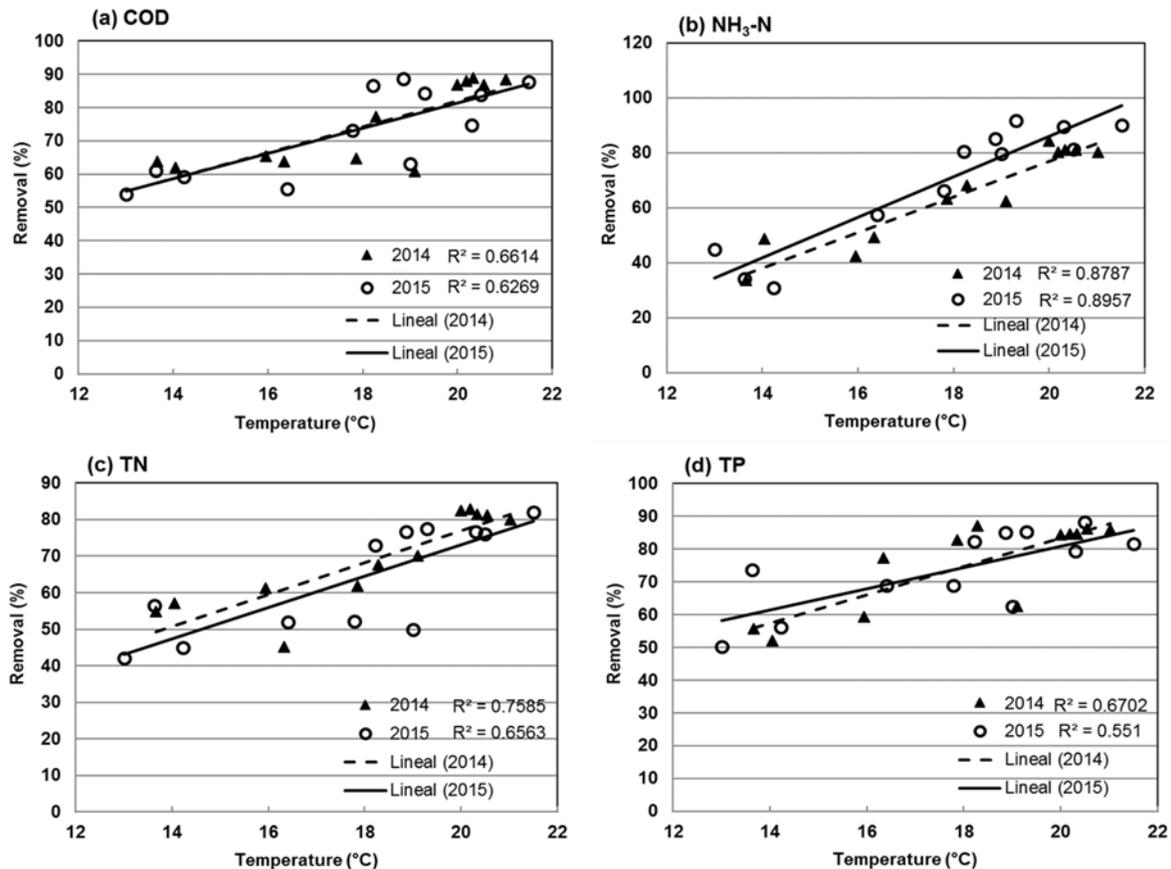
Figure 3: Removal rates variation of (a) COD, (b) NH₃-N, (c) TN, and (d) TP, during 2014 and 2015 and 2015



There was no significant difference ($P>0.05$) in the COD removal rate between 2014 and 2015. The regression analysis between the temperature of the water and the COD removal rate yielded a R^2 value of 0.661 in the year 2014, and of 0.626 in 2015 (Figure 4a). In general, in the various studied years, the relationship between the COD removal rate and the temperature was moderately strong. The results obtained in this research agree with those of other researches⁽²⁸⁾; those authors studied the efficiency of a wetland in removing organic

matter and nutrients from an effluent of a pig farm and they determined a COD removal rate of 90 %; however, the levels obtained the rest of the year were lower than those estimated by this research.

Figure 4: Linear regression and determination coefficient between the pollutant removal rate and the water temperature (a) COD, (b) $\text{NH}_3\text{-N}$, (c) TN and (d) TP in 2014 and 2015



Although the results of the removal rate coincide, there are differences in the HRT, as these authors used only two days, whereas in the present research the HRT was 10 d – a considerable difference (8 d) in the time of exposure to the nutrient in the system. Another difference in regard to the present research was the COD concentration in the influent; those authors used concentrations of 1,000 to 1,400 mg L^{-1} , whereas in the present research the influent showed little variability, having been $835 \pm 64 \text{ mg L}^{-1}$ in 2014 and $774 \pm 26 \text{ mg L}^{-1}$ in 2015. The authors ascribed the efficiency of the wetland to several factors, such as the season of the year, as the maximum removal rates in the assessed parameters were attained in the summer.

On the other hand, other techniques have been utilized to try to increase the removal rate of pollutants in wetlands; several authors⁽³²⁾ assessed the effect of the application of oxygen to a surface flow wetland, obtaining an increase of 20 % in the organic matter removal rate. However, other processes, such as nitrification, were also negatively affected, as no significant NH₃-N removal rate increase (27-48 %) was obtained in the wetland.

The results for NH₃-N removal are shown in Figure 3b. In 2014, the mean annual NH₃-N removal rate was 65 ± 17 %. The lowest removal rate (34 %) was observed in December, when the average temperature was 14 °C. The maximum NH₃-N removal rate (84 %) was obtained in June, with a mean temperature of 20 °C. In 2015, the average removal rate was 69 ± 22 %. The minimum value observed (31 %) occurred in January, with a temperature of 14 °C, while the maximum value (92 %) was obtained in August, with a mean temperature of 19 °C. The variance analysis showed a significant difference ($P < 0.05$) between the NH₃-N removal rate at different temperatures in 2014. That same year, a significant ratio ($P < 0.05$) was estimated between the temperature and the NH₃-N removal efficiency, with a R^2 of 0.895. For the year 2015, the linear regression showed a R^2 of 0.878 (Figure 4b). NH₃-N removal was lower than 70 % when the temperature of the water was below 20 °C. Conversely, when the temperature was equal to or higher than 20 °C, the removal rate increased gradually until reaching levels above 80 % in almost all the cases, amounting to a 10 % increase for each added degree of water temperature.

The NH₃-N reduction obtained in this research differed from that obtained in other studies. Other researches⁽¹⁴⁾ reported a 52 % removal rate. Other studies⁽¹²⁾ obtained a 100% NH₃-N removal rate; however, these studies were performed at pilot scale with controlled environmental conditions, which influenced the results. The results obtained in this research were similar to those obtained by other authors⁽¹³⁾, as a NH₃-N removal rate of approximately 85 % was estimated when assessing the efficiency of a surface flow wetland in southern Texas, USA, during the summer of 2008.

These results also agree with those mentioned by different authors⁽³⁵⁻³⁸⁾ who highlight the importance of temperature in ammonium removal from the wetlands. According to them, at low temperatures (5–10 °C), biological processes such as denitrification can be drastically inhibited. In general, the processes that take place in the nitrogen cycle are inhibited under cold climate conditions, as the amount of available oxygen diminishes considerably, and therefore the concentration of bacteria also decreases under extreme temperature conditions⁽³⁸⁾. The arguments mentioned by these authors coincide with the results obtained in this research, as the NH₃-N reduction was greater at higher temperatures and dwindled considerably in the cold season.

Figure 3c shows variability in the TN removal rate for the years 2014 and 2015. In 2014, the average TN removal rate showed a value of 69 ± 13 %. The minimum removal rate (45 %) occurred in February with a mean temperature of 16 °C. The maximum removal rate (82 %) was observed in June, when the mean temperature was 20 °C. In 2015, an average removal

rate of 63 ± 15 % was obtained. The minimum value was observed in December (42 %), corresponding to a mean temperature of the water of 13 °C, while the highest value (82 %) occurred in May, with an average temperature of 22 °C. The mean TN removal rate obtained in this research is below that reported by other studies⁽²²⁾ where averages of 95 to 98 % TN removal were obtained. However, their experiments used wastewater from aquaculture and from a combination of different types of wetlands. Other factors like the design of the wetland are important and have a direct impact on the efficiency of the system; for example, the results of other studies⁽²⁰⁾ have suggested that HRT is one of the most important factors for TN removal; they proved that the TN removal rate can increase to up to 99 % with a 6 to 8-day HRT.

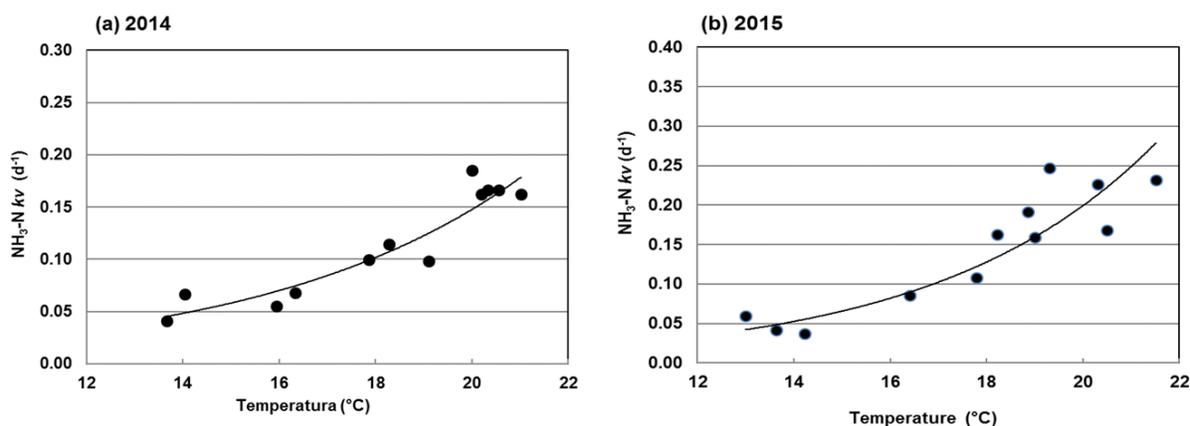
The statistical analysis showed that there are no significant differences ($P>0.05$) between the TN mean removal rates for the years 2014 and 2015. As for the effect of the temperature on the efficiency of TN removal, in the year 2014 a high determination coefficient ($R^2=0.758$) was obtained, while in 2015 this coefficient decreased slightly ($R^2=0.656$), indicating a moderately strong relationship between the temperature and the TN removal rate, with a 95% confidence interval (Figure 4c).

Figure 3d shows the variability of the TP removal rate in the years of the study. The mean TP removal rate in 2014 was 75 ± 13 %, while in 2015 it was estimated in 73 ± 12 %. In the year 2014, the minimum value was obtained in January (52%), with a mean temperature of the water of 14 °C. The maximum removal rate (75 %) was observed in April, with a mean temperature of 18 °C. In 2015, the mean removal rate was 73 ± 17 %. The minimum value (50 %) occurred in December with a mean temperature of 13 °C, and the maximum value (88 %) was obtained in September, with a mean temperature of 20 °C. The statistical analysis showed that there are no significant differences between the two years analyzed in this study (2014 and 2015). Figure 4d shows the linear regression of the obtained data; in the year 2014, the determination coefficient was $R^2=0.670$, indicating a moderately strong relationship between the TP removal rate and the temperature of the water in the wetland. As for the year 2015, the regression analysis yielded a determination coefficient of $R^2=0.551$. The results obtained in this research are above those reported in other studies, where a TP removal rate of 45 % was estimated⁽³⁹⁾. Another author⁽²⁷⁾ also reported a lower TP removal rate than the one obtained in the present study: he estimated an acceptable TP removal rate of 21 to 44 % in temperatures below 10 °C. This agrees with the results obtained by various authors, according to whom the P removal rate is less affected by the temperature due to the prevalence of the adsorption processes and sedimentation, as opposed to the biological processes. A large number of wetlands have been proven to operate less efficiently in a cold climate than in temperate climates⁽³⁸⁾. Studies carried out in China at an ambient temperature of 4 °C and in Norway at 20 °C exhibited an acceptable reduction of pollutants when the wetland was artificially isolated from nature⁽³⁶⁾.

Reaction rate constant and coefficient of temperature of ammonia nitrogen

Figures 5a and 5b show the relationship between k_v and the monthly temperature of the water in the system for $\text{NH}_3\text{-N}$ during the years 2014 and 2015. The volumetric reaction rate constant ($k_v \text{ d}^{-1}$) in 2014 ranged between 0.041 and 0.185 d^{-1} at mean temperatures of 13 °C to 21 °C in the wetland. It was evident that the k_v value increased exponentially with the increased temperature of the water. On the other hand, in 2014 k exhibited a mean value of 2.60 cm d^{-1} , and in the year 2015 the estimated value was 3.22 cm d^{-1} . The results obtained for k in the research were below those reported by another study⁽¹¹⁾ carried out in Taiwan, where a value of $k=6.26 \text{ cm d}^{-1}$ was estimated in a surface flow wetland. However, the $\text{NH}_3\text{-N}$ concentration in the influent demonstrated a significant variability during the study (1-26 mg L^{-1}). Conversely, in the present study, the $\text{NH}_3\text{-N}$ concentration remained constant, with little variability ($33 \pm 2.4 \text{ mg L}^{-1}$ in 2014 and $36 \pm 4.5 \text{ mg L}^{-1}$ in 2015).

Figure 5: Ratio between k_v and monthly temperature for $\text{NH}_3\text{-N}$ during 2014 and 2015



Conclusions and implications

This study proved the capacity of a SFCW for the reduction of pollutants like COD, $\text{NH}_3\text{-N}$, TN and TP in wastewater from a pig farm. During the study period (2014 and 2015), the wetland showed an acceptable efficiency in the reduction of the assessed pollutants; however, in the specific case of $\text{NH}_3\text{-N}$, the estimated removal rate was less than 60 % in the season with the lowest temperature, and above 75 % in the warm season, evidencing seasonal patterns in the removal rate. Unlike the case of $\text{NH}_3\text{-N}$, the COD and TP removal rates exhibited little variability during the period in which the system operated. The removal rate

of ammonium exhibited the greatest dependency on the temperature of the water. When the temperature of the water was above 17 °C, the vegetation grew faster, which also increased microbial activity and the NH₃-N removal rate, and was significantly higher than when the temperature of the water was below 17 °C. It is recommended to evaluate other parameters such as the air temperature, the precipitation and the evaporation directly at the site in order to assess their effect on the behavior of the wetland.

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