Reduction of hydrogen sulfide by recirculation of effluents in stabilization ponds with the presence of microalgae

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Abstract

Stabilization ponds (SPs) are used as an alternative for wastewater treatment; however, one of their disadvantages is the emission of bad odors caused by hydrogen sulfide (H₂S), which is highly toxic and corrosive, in addition to causing damage to the health of the surrounding population and negatively affecting the metallic structures and electrical equipment exposed. This problem is a priority to be solved in order to continue with the operation of wastewater treatment plants. In this study, a procedure based on the recirculation of 20% of the effluent, which contains native microalgae, is presented as a solution alternative. To determine the optimal percentage of effluent recirculation, a series of recirculation tests were implemented through the jar method and subsequently it was taken to a macro scale, evaluating the performance of the effluent recirculation, comparing the monthly averages of 2019 before the implementation of the project with 2020 already operating. The results showed significant changes in the percentages of pollutant removal, in the biochemical oxygen demand, of 20.8%, total suspended solids, 22.17%, fats and oils, 29.5% and a reduction in fecal coliforms, 91.4%, in addition to reducing H₂S with 48.9%, which reduces unpleasant odors and the potential toxic effect on health. We can conclude that the methodology is efficient in improving the parameters, thus complying with the standards of the applicable regulations.

Keywords: effluent recirculation, wastewater treatment.

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Introduction

SPs are a type of wastewater treatment (WWT) system consisting of artificial ponds that require long hydraulic retention times that improve water quality, this type of treatment is recommended in countries with tropical climates, since environmental conditions increase the efficiency in the removal of pollutant (Coggins et al., 2019). SPs can be classified in relation to the presence of oxygen into three types: anaerobic, facultative and maturation (Edokpayi et al., 2021). In the anaerobic ones, the bacteria present do not require dissolved oxygen for the decomposition of organic matter, since this is degraded by methanogenic processes, facultative ponds are characterized by the presence and absence of dissolved oxygen, having an aerobic process in the upper layer and anaerobic conditions in the lower layer (Joshi et al., 2020).

While maturation ponds have little depth, thus being a totally aerobic process. Their design has three main objectives. The elimination of fecal coliforms and pathogenic microorganisms, which represent a serious health hazard, causing diseases such as: hepatitis, cholera and typhoid, among other important ones (Achag et al., 2021), removal of nutrients: nitrogen and phosphorus, in order to avoid eutrophication in the receiving bodies (Laaksonen et al., 2017) and finally the removal of organic matter also called biochemical oxygen demand (BOD₅), responsible for the depletion of dissolved oxygen necessary for the maintenance of aquatic ecosystems (Minakshi et al., 2018). The result of the final effluent of the WWT must comply with the water quality referred to in NOM-001-SEMARNAT-1996, which indicates the maximum permissible limits (DOF, 1996).

The main advantages of SPs are their low construction, operation and maintenance costs compared to other WWT systems, which is why it is the most frequently used system in small municipalities and regions with large areas available (Al-Zreiqat et al., 2018). SPs are well accepted in developing countries because they are economically viable (López et al., 2018). However, a disadvantage of SP systems is that they generate a socioenvironmental problem; due to the bad smell caused by the decomposition of organic matter in anaerobic ponds (Ho et al., 2018).

The bad smell generated in SPs is caused by the generation of H₂S, derived from the presence of sulfates in the wastewater, where the sulfate-reducing anaerobic bacteria use the oxygen of the sulfates, generating this acid, which produces the smell of rotten egg and mercaptans (Ramazan, 2021), which can be a real nuisance for communities and residents, who coincide in the reception of winds from treatment plants. It is important to mention that H₂S, beyond the odor, is a highly corrosive agent and causes damage to the structural integrity of WWT facilities and it is known that this compound in contact with living beings is highly harmful because it has been reported that it can cause from headaches to death (Sun et al., 2019; Salehi and Chaiprapat, 2019).

For this reason, there is a need to make a modification in the design of SPs in which it is proposed to apply a reengineering to the WWT by implementing a recirculation of the effluent at the beginning of the process, achieving the following advantages: avoid the generation of odors by reducing the concentration of H₂S, control the seasonal variations of the main
parameters, maintain aerobic conditions at the entrance of the first pond (Liu, 2018). Based on the above, the objective of this study was to improve the current system of stabilization ponds in the municipality of Torreón, Coahuila, through the execution of a process of recirculation of 20% of the effluent to the primary ponds, determining parameters of water quality (pH, electrical conductivity, BODs, total suspended solids, dissolved oxygen, fats and oils, fecal coliforms, helminth eggs and generation of H₂S.

**Materials and methods**

**Study area**

The SPs of this study are in the municipal wastewater treatment plant (WWTP) of Torreón Coahuila, Mexico, at 25° 30’ 50.3” north latitude; 103° 19’ 16.8” west longitude and 1 125 masl. The study was conducted during the period from January to December 2019 and 2020 (Figure 1).

![Figure 1. Jar equipment.](image)

**Determination of the percentage of return**

To determine the percentage of the effluent, a preliminary experiment was carried out by means of tests by the jar method (Leones et al., 2018), in 1 L beakers (Figure 1) jar equipment, model TS1198X85, Thomas Scientific brand, which consisted of making mixtures of the influent and effluent with different percentages of recirculation 10, 20 and 30% respectively, to know the optimal percentage of water quality without impacting operating costs.

**Stages of the study**

In the present study, two stages were carried out; stage 1, 20 monitoring points were determined at intervals of 100 m in the periphery of the WWTP, in which measurements of H₂S levels were carried out (Figure 2).
Figure 2. Map of the study area, the image shows a satellite view of the municipal wastewater treatment plant of the city of Torreón, Coahuila, where the twenty sampling sites are indicated with red dots. The facilities are in the Villas de Zaragoza neighborhood, the geographical coordinates of the site are 25° 30’ 50.3” north latitude; 103° 19’ 16.8” west longitude and 1 125 masl (image taken from Google Earth).

Stage 2, water samples were taken according to NOM-001-SEMARNAT-1996, every 15 days for 24 months, from the influent and effluent, in which the parameters of pH, electrical conductivity (E.C.), biochemical oxygen demand (BOD₅), total suspended solids (TSS), dissolved oxygen (DO) and fats and oils, fecal coliforms, helminth eggs and generation H₂S were determined.

Analytical methods

The above parameters were determined using the methodologies proposed by the standard methods for the examination of water and wastewater (Rice et al., 2012). The pH values were obtained by a potentiometer (ultra BASIC series meter; Denver, Colorado. USA), electrical conductivity (E.C.) using a conductivity meter (Hanna HI 993310 Ann Arbor, Michigan. USA). The biochemical oxygen demand (BOD₅) was determined according to NMX-AA-030/1-SCFI-2012 with a dissolved oxygen probe (Orion, thermo scientific), the total suspended solids (TSS) were determined by porcelain evaporation capsules, using a Gooch crucible filtration device according to the (Secretaría de Economía, 2015), for dissolved oxygen (DO), it was determined according to the (Secretaría de Economía, 2001), using the same probe as in the determination of BOD₅, for the determination of fats and oils, an extraction equipment (Soxleth Fermatte) was used according to the standard of the Secretaría de Economía, 2013, for fecal coliforms, they were determined by the most probable number (MPN) technique, according to the standard of the Secretaría de Economía (1987), for the determination of helminth eggs, the screening technique was used according to the standard of the Secretaría de Economía, 2012.

And for the determination of the H₂S concentration, a GasAlertMax XT II gas detector (Honeywell, United States of America) with 0-200 ppm measurement ranges and 1 ppm resolution was used. The calibration of the equipment was according to the manufacturer’s specifications.
Data analysis

The results obtained were analyzed using a statistical analysis of means, standard deviation and a Student’s t test ($\alpha=0.05$) (Walpone et al., 2012). These results were the product of a monthly sampling at each point, these samples were carried out for two years for comparative effects, before recirculation (2019) and after recirculation (2020).

Results and discussion

Twenty percent of the total effluent of the WWTP was considered as the optimal percentage for the recirculation, this was determined by a preliminary test by the jar test (Table 1). For the analysis of the results, the values prior to the recirculation of the influent and effluent (2019) were contrasted with respect to the values after it (2020).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Influent</th>
<th>10% test</th>
<th>20% test</th>
<th>30% test</th>
<th>40% test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Stdev</td>
<td>Mean</td>
<td>Stdev</td>
<td>Mean</td>
</tr>
<tr>
<td>Fats and oils (mg L(^{-1}))</td>
<td>82.25 ±7.4</td>
<td>71 ±9.5</td>
<td>55.8 ±3.4</td>
<td>51 ±4.1</td>
<td>46.8 ±4.4</td>
</tr>
<tr>
<td>BOD5 (mg L(^{-1}))</td>
<td>300 ±16.9</td>
<td>274.6 ±0</td>
<td>230.9 ±0</td>
<td>215.3 ±0</td>
<td>188.8 ±0</td>
</tr>
<tr>
<td>TSS (mg L(^{-1}))</td>
<td>281.9 ±15.3</td>
<td>266.4 ±0</td>
<td>228.3 ±0</td>
<td>193.2 ±0</td>
<td>178.5 ±0</td>
</tr>
<tr>
<td>DO (mg L(^{-1}))</td>
<td>0 ±0</td>
<td>0.35 ±0.15</td>
<td>1.45 ±0.45</td>
<td>1.65 ±0.45</td>
<td>1.9 ±0.4</td>
</tr>
<tr>
<td>H(_2)S (mg m(^{-3}))</td>
<td>22.5 ±4.9</td>
<td>12 ±2</td>
<td>7.5 ±1.5</td>
<td>5.5 ±1.5</td>
<td>4 ±1</td>
</tr>
<tr>
<td>pH</td>
<td>6.9 ±0</td>
<td>7.3 ±0.1</td>
<td>7.65 ±0.25</td>
<td>8.05 ±0.15</td>
<td>8.3 ±0.2</td>
</tr>
<tr>
<td>Conductivity (mS cm(^{-1}))</td>
<td>101.7 ±11.9</td>
<td>95.4 ±7.3</td>
<td>97.4 ±10.7</td>
<td>92.75 ±8.45</td>
<td>90.9 ±8.5</td>
</tr>
</tbody>
</table>

pH variation

Before recirculation, the average pH value in the influent was 7.5 ±0.2, while in the effluent, in the same period, it had an annual average of 8.3 ±0.2. After the recirculation of 20%, the results obtained were annual averages of 7.2 ±0.2 for the influent and 8.2 ±0.3 for the effluent (Figure 3).

**Figure 3. Results of the potential of hydrogen, before and after the recirculation of the influent and effluent.**
No significant differences between the results before and after recirculation were found. It is considered that this was mainly due to the natural variations of the wastewater generated in the municipality, this is very relevant because the variation of the pH considerably affects the structure of the microbial communities and therefore causes a fluctuation in the production of H$_2$S. However, these pH ranges continue to be ideal for other wastewater treatment processes (Leite et al., 2020) and it is important to mention that these values are also optimal for a future nitrogen and phosphorus recovery process (Kuzumita et al., 2020).

**Variation of EC**

The value of the annual average for the EC of 2019 in the effluent, before recirculation, was 100.8 ±8.6 mS cm$^{-1}$, while in 2020, after recirculation, an average of 103.7 ±9 mS cm$^{-1}$ was obtained. No significant differences before and after recirculation were found, nor effect on the process of generation of H$_2$S.

**Biochemical oxygen demand**

The value of the annual average for the BOD$_5$ of 2019, before recirculation, was 231.7 mg L$^{-1}$, while in 2020, after recirculation, an average of 83.1 mg L$^{-1}$ was obtained. The removal percentages for BOD$_5$ ranged from 56.5 to 64.7% and after recirculation (Table 1), the averages ranged from 34.2 to 60.5. For 2020, the averages ranged from 50.1 to 93.1, with an average of (78 ±15.2%) in June. At the international level, values ranging between 20.2 and 85.1 have been reported (Verbyla, 2016), which indicates that the recirculation in the present work improved the removal of BOD$_5$ (Figure 4), more markedly for 2020, except for January, the values were higher in the other months prior to recirculation in 2019 (Ávila et al., 2017).

![Figure 4. Results of the biochemical oxygen demand, before and after the recirculation of the influent and effluent.](image)
They obtained higher values but this was due to the quality of the water they used, in addition to using a percentage of recirculation much higher than ours (50%), on the other hand, their study also proves that the efficiency of the technique can decrease between 10 and 15%, depending on the season of the year, obtaining better in summer compared to winter (Minakshi et al., 2017), it uses recirculation ranges between 25 and 75%, seeing that, with this last percentage, the removal of BOD was much better, but significant changes in the decrease in contaminants begin to be noticed with only 25% recirculation.

**Total suspended solids**

The value of the annual average for the TSS of 2019, before recirculation, was 114.3 mg L\(^{-1}\), while after recirculation in 2020, it was 89 mg L\(^{-1}\) (Table 1). The removal percentages obtained for TSS for 2019 ranged from 35.1-80.5% before recirculation and 27.1-60.9% after recirculation. Although the improvement was not so evident in 2019, by mid-2020, the situation was improved with removal values of 66.8-91% (Table 2). Published studies have determined that the percentages fluctuate with values from 25.7-86% (Verbyla, 2016).

**Table 2. Statistical means of the treated water quality parameters of 2019 before recirculation and 2020 after recirculation.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2019</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Stdev</td>
</tr>
<tr>
<td>Fats and oils (mg L(^{-1}))</td>
<td>Influent</td>
<td>56.32 ±14.37</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>19.67 ±3.96</td>
</tr>
<tr>
<td>Total suspended solids (mg L(^{-1}))</td>
<td>Influent</td>
<td>256.53 ±14.69</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>114.34 ±21.2</td>
</tr>
<tr>
<td>BOD(_5) (mg L(^{-1}))</td>
<td>Influent</td>
<td>231.68 ±49.66</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>105.04 ±24.5</td>
</tr>
<tr>
<td>Fecal coliforms (E06)</td>
<td>Influent</td>
<td>7.14 ±0.68</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>54.3 ±0.8</td>
</tr>
<tr>
<td>Potential of hydrogen</td>
<td>Influent</td>
<td>7.45 ±0.24</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>8.28 ±0.29</td>
</tr>
<tr>
<td>Dissolved oxygen (mg L(^{-1}))</td>
<td>Influent</td>
<td>0.06 ±0.09</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>7.18 ±1.45</td>
</tr>
<tr>
<td>Helminth eggs (MPN)</td>
<td>Influent</td>
<td>7.83 ±2.11</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>3.75 ±1.19</td>
</tr>
<tr>
<td>Electrical conductivity (mS cm(^{-1}))</td>
<td>Influent</td>
<td>111.54 ±8.58</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>100.8 ±9.91</td>
</tr>
</tbody>
</table>

**Dissolved oxygen**

The value of the annual average for the DO of 2019, before recirculation, was 7.2 mg L\(^{-1}\), while in 2020, post-recirculation, it was 7.9 mg L\(^{-1}\). Unlike other measured parameters, the increase in the concentration of dissolved oxygen is a remarkable and positive result, since, in this way, the...
inhibition of the growth of anaerobic bacterial communities is achieved, which are responsible for the production of H₂S; therefore, the harmful effects of this compound and therefore the bad odors decrease considerably (Aslam et al., 2019). The observed increase is due to the increase in the concentration of algae (Jørgensen, 2020).

**Fats and oils**

The value of the annual average for fats and oils of 2019 in the effluent, before recirculation, was 19.7 mg L⁻¹, while in 2020, after recirculation, a decrease of 70.4% was obtained. According to the results found, the reduction values from influent to effluent during 2019 began with 43.5%, these values were increasing after the recirculation process to 83.5% in 2020.

This increase of about 40% is mainly due to two factors, the increase in dissolved oxygen favors the development of aerobic bacteria and increases their metabolic activity, which increases the rate of removal of contaminants (Holmes et al., 2019), on the other hand, recirculation increases the hydraulic retention period, which in turn increases the contact time of lipophilic bacteria with fats and oils, enhancing their degradation (Cisterna, 2015).

**Fecal coliforms**

The value of the annual average for FC of 2019 in the effluent, before recirculation, was 4.5 E04 MPN 100 ml⁻¹, while in 2020 after recirculation, an average of 4.8 E04 MPN 100 ml⁻¹ was obtained. This increase is due to the natural variations of the influent since, in 2019, there was an average value of 7.14 E06 with a removal of the order 99.369%, requiring a removal greater than 99.985% to comply with the provisions of NOM-SEMARNAT-1996 (this without recirculation).

In 2020 with the recirculation, the average value of the influent was 8.97 E06 with a removal of the order of 99.46%, which is almost a decimal unit, which in exponential removal of fecal coliforms is very significant. This effect is due to the same causes presented in the parameters of DO and fats and oils. These results are superior to those reported in studies of coliform reduction models in 186 maturation ponds worldwide (Rezvani et al., 2021). Several studies presented levels of reduction of this indicator in averages of 23-99% (Sheludchenko et al., 2016; Verbyla et al., 2016), where one of these studies presented lower values (23-43%) than those found in our study in 2020 (Reinoso et al., 2011). This indicates that the stabilization ponds meet the objective of pathogen reduction.

In the parameter of fecal coliforms, although it is still above the standard, the reduction presented in this study is considerable and in conjunction with other types of systems (chemical or homogenization curtains) (Cortés, 2013), the combination of both processes could achieve compliance with the applicable regulations without requiring heavy investments.

**Helminth eggs**

The helminth egg parameter also had a significant result, decreasing almost by half after recirculation. The value of the annual average for helminth eggs in 2019, before recirculation, was 3.75 E/L, while in 2020, after recirculation, it was 1.83 E/L. This reduction of almost 50% is
remarkable, although it is true, prior to recirculation, this parameter was below the maximum permissible limit, which is 5 E/L, and given its behavior in a stratified water column, it is expected that the recirculation coupled with a process of physical homogenization, such as flow reduction curtains, will achieve their total elimination (Benito et al., 2020).

**Generation of H₂S**

Emissions of gases such as H₂S are responsible for bad odors and were significantly reduced during the samplings of 2020 ($p=0.01$). The results were statistically different comparing the before and after recirculation, obtaining an average annual reduction of 48.9% of H₂S (µg L⁻¹) v/v. Achieving that the parameter is within the permissible limits indicated in the standard of the Secretaría del Trabajo y Previsión Social (1999). From the chemical point of view, the recirculation of the effluent inhibited the generation of H₂S in the anaerobic ponds, since the added effluent contained a greater number of microalgae and calcium carbonates, which contributes to the elimination of the microbiota by alkalinization of the medium.

It is important to emphasize that the methanogenic microbiota is acidophilic and, therefore, competition with microalgae prevents its development and the generation of H₂S responsible for bad odors, this phenomenon causes a sealing effect since, in the upper layers, an alkaline environment with more oxygen is generated and due to this stratified arrangement, the lower layers do not suffer alterations in their traditional functioning, since the anaerobiosis and the natural microbiota do not change and continue to work with the same efficiency of removal of other contaminants (Aslam et al., 2019; Sun et al., 2019; Salehi and Chaiprapat, 2019).

The recirculation allows the concentration of H₂S to decrease considerably, although this compound is not a greenhouse gas, it is estimated that other gases also decrease their production with this reengineering, such as the greenhouse gases that are produced in the WWTP (methane, carbon dioxide), although it is not the objective of this study, it would be advisable to determine the decrease in the concentration of these gases, evaluating recirculation as an alternative for the mitigation of climate change due to the greenhouse effect in SPs (Figure 5).

**Figure 5. Concentration mg m⁻³ of production of H₂S.**
Conclusions

The recirculation of 20% of the effluent significantly reduced ($p = 0.05$) the values of fats, oils, fecal coliforms, helminth eggs and generation of H$_2$S. This allowed compliance with the parameters of fats and oils in Mexican regulations. It is also important to mention that the concentration of H$_2$S decreased at the 20 sampling points; however, this pollutant is not regulated in Mexican environmental legislation even though its toxicity is reported in international literature.

On the other hand, although there was a considerable reduction in the concentration of coliforms, this parameter is still out of the standard, which is to be expected since its initial concentration was high and, given the nature of this type of treatment, it is difficult to achieve the concentration stipulated in the standard, it is important to note that even other types of treatments do not manage to lower the concentration of coliforms to comply with the standard, therefore, they must resort to chemical disinfection processes.

In view of the results obtained, recirculation represents a viable alternative from the economic and ecological point of view since it reduces operating costs, and in terms of environmental health reduces the risk of exposure to toxic gases in the surrounding population. It is advisable to continue the evaluation for a longer period, since only one year was evaluated, its continuation being interesting to continue analyzing the effects of recirculation in the face of natural and seasonal variations of the influent.

Cited literature


