Tratamento terciário de lixiviado em banhados construídos cultivados com oleaginosas

Leachate tertiary treatment using wetlands cultivated with oilseeds

João Antônio Monteiro Florêncio¹
Lucas Zanon ScheroltⅡ
Viviane TrevisanⅢ
Everton SkoronskiⅣ

Abstract
The objective of this study was to evaluate the efficiency of the wetlands cultivated with sunflower and soybean in the removal of Chemical Oxygen Demand, ammonia, nitrate, nitrite, total phosphorus and Kjeldahl Total Nitrogen (KTN) of the treated leachate from the landfill treatment plant of the city of Lages / SC. It was also analyzed the plants development as a function of the effluent applied in the wetlands compared to wetlands irrigated with chemical fertilizer. The wetlands were operated in batch with hydraulic retention times (HRT) of 2 and 4 days, receiving treated slurry in concentrations of 10 and 25% and liquid chemical fertilizer (5 ml / L). In the tests carried out with HRT of 4 days only the concentrations of COD and of ammonia were analyzed. After 4 months, the plants size was measured to verify their growth. In the tests carried out with the soybean there was no germination of the seeds. In both HRT tested, a greater removal of phosphorus, ammonia, nitrite and KTN was observed when 25% concentration of leachate. It was observed that the sunflower plants showed a higher size when cultivated in wetlands operated with HRT of 4 days and that they received the treated leachate in the concentration of 10%.

Keywords: Wetlands; Sunflower; Leachate

Resumo
O objetivo deste estudo foi avaliar a eficiência do uso de banhados construídos cultivados com girassol e com soja na remoção da Demanda Química de Oxigênio, amônia, nitrato, nitrito, fósforo total e Nitrogênio Total Kjeldahl do chorume tratado proveniente da estação de tratamento do aterro sanitário da cidade de Lages/SC. Também foi analisado o desenvolvimento das plantas em função do efluente aplicado no banhado em comparação com banhados regados com adubo químico. Os banhados foram operados em batelada com tempos de detenção hidráulico (TDH) de 2 e 4 dias,

¹ Graduando Engenharia Ambiental e Sanitária, Universidade do Estado de Santa Catarina, Lages, SC, Brasil - joao_antonio_monteiro@hotmail.com
Ⅱ Graduando Engenharia Ambiental e Sanitária, Universidade do Estado de Santa Catarina, Lages, SC, Brasil. szanonnn@gmail.com
Ⅲ Doutor, Departamento de Engenharia Ambiental e Sanitária, Universidade do Estado de Santa Catarina, Lages, SC, Brasil. viviane.trevisan@udesc.br
Ⅳ Doutor, Departamento de Engenharia Ambiental e Sanitária, Universidade do Estado de Santa Catarina, Lages, SC, Brasil. everton.skoronski@udesc.br
recebendo chorume tratado nas concentrações de 10 e 25% e adubo químico líquido (5 ml/L). Nos ensaios realizados com TDH de 4 dias foram analisadas apenas as concentrações de DQO e de amônia. Após 4 meses, mediu-se o tamanho das plantas para verificar seu crescimento. Nos testes realizados com a soja não houve germinação das sementes. Em ambos os TDH testados, observou-se uma maior remoção de fósforo, amônia, nitrito e NTK quando foi aplicado chorume na concentração de 25%. Observou-se que as plantas de girassol apresentaram maior tamanho médio quando cultivadas nos banhados operados com TDH de 4 dias e que receberam o chorume tratado na concentração de 10%.

**Palavras-chave:** Banhados construídos; Girassol; Chorume
1 Introduction

The landfill leachate can be considered as a matrix of extreme complexity, composed by four fractions: dissolved organic matter, represented by volatile fatty acids; humic and fulvic compounds; xenobiotic organic compounds, represented by aromatic hydrocarbons; inorganic macro-components such as calcium, magnesium, sodium, potassium, ammonia, iron, etc. and potentially toxic metals. The conventional processes used in leachate treatment are based on physical-chemical and biological processes. The first, are usually based on precipitation-flocculation processes which present high purification efficiency only for suspended substances. In addition, the contaminants are not completely degraded, which necessarily implies the generation of a solid phases (sludge) (Tchoubanoglo & Kreith, 2002). Biological processes can be used to leachate treatment. Unfortunately, characteristics such long detention times, from days to weeks, and low efficiency in the recalcitrant compounds and pigments removal, make their efficiency quite controversial (Tchoubanoglous & Kreith, 2002).

To increase the efficiency of the pollutant compounds removal in the leachate, the wetlands as a low-cost alternative for this purpose. In the wetlands, physical (sedimentation, filtration and adsorption), chemical (decomposition) and biological (microbial metabolism, plant metabolism and natural decay) mechanisms of pollutant removal are performed (Jordão and Pessoa, 2005). The wetlands can be classified as a natural system of wastewater treatment, based on saturated areas by water or groundwater, where several species of plants that depend directly on the nutritional characteristic of the region where they found (Wood & McAtamney, 1996). These systems were created to optimize the removal or transformation of pollutants from wastewater, in addition to creating an environment to the development of different types of vegetation. Vertical flow baths operate with intermittent vertical flow of wastewater, are filled with gravel and sand and the level of the applied liquid remains below the support medium. (Kadlec, 1995).
The use of wetlands provides greater operational control with regard to wastewater purification, appearing as an environmentally more adequate alternative. They also have advantages when compared to natural systems, emphasizing the need for a smaller surface to treat the same load and the fact that they are more easily applied to specific effluents. (Porchaska and Zouboulis, 2006). The good results of wetlands in the leachate treatment are already known internationally. The suspended solids present in the leachate can be rapidly removed by the process, due to the conditions of tranquility of flow that determines the deposition of these materials. Growth and microbial activity are responsible for the removal of soluble organic matter. The removal of total nitrogen can reach 70% efficiency, not only by the incorporation into the aquatic macrophytes fabric but also by the nitrification and denitrification processes that take place inside the wetland (Bidone, 2008).

Studies conducted by Fleck (2003), treating leachate in wetlands, obtained removals of 42.5% of organic matter, 36.7% of phosphorus, 77.5% for total suspended solids and overall removal of 37.7% for all forms of nitrogen.

Beltrão (2006) also used wetlands for leachate treatment, obtaining efficiencies above to 46% in the removal of organic matter.

In the wetlands, the plants and the support medium allow the accumulation and the fixation of the active biomass in the system. As a result of their activity, the plants introduce oxygen into the liquid medium forming an environment favorable to the aerobic stabilization of the organic matter. Plants develop from the consumption of nutrients, which were presents in the liquid to be treated and can be assimilated by plants (Bidone, 2008).

Ruttens et al. (2011) report a great tendency in the use of oil plants as phytoextractors of heavy metals and biomass producers for transformation into biodiesel, contributing to the decontamination of polluted areas and to the production of energy that is less polluting to the environment. Good phytoextraction results were obtained using species such as castor bean (Romeiro et al., 2006), sunflower (Zeittouni et al., 2007) and maize (Pereira et al., 2007).
Oleaginous plants have a large quantity of oil, both from their seeds (soybean, rape, sunflower) and from their fruits (palm, coconut), and can be used for the production of vegetable oil. Another important characteristic of some of these plants is the fact that after the extraction of the oil, by-products can be used for different applications. In Brazil, with the model adopted for the development of the Biodiesel Program, the production chain of this biofuel uses oilseed species as its main raw material. The diversity of agricultural crops (oilseeds) used varies according to the characteristics of each Brazilian region or State (Ministério do Meio Ambiente, 2006).

The development of agroenergy production chains of different oilseeds needs to take into account factors that involve the environment in order to indicate the best cultivars to be explored. For the South Region the oil plants with the greatest potential for cultivation are soya, rape, sunflower and cotton (Ministério do Meio Ambiente, 2006).

From an economic point, the viability of biodiesel is related to the establishment of a favorable equilibrium to the Brazilian trade balance, since diesel is the most consumed petroleum derivative in Brazil, and that a growing fraction of this product is being imported annually. Data from the National Petroleum Agency (ANP) (2005) indicate that Brazil imports 9% of the total diesel oil it consumes. However, this percentage rises to 15% when oil imports are taken into account, since diesel accounts for approximately 35% of the total refined volume. In environmental terms, the adoption of biodiesel, even if progressively, from 2 to 5% additions in petroleum diesel, will result in a significant reduction in particulates emissions, sulfur oxides and the greenhouse effect (Mitellbach, 1990; Koverski and Hess, 2006).

In the present study were evaluated the efficiency of wetlands used in the tertiary treatment of leachate from the landfill of the city of Lages / SC and the cultivation of oleaginous plants in these wetlands for the biodiesel production. These results will serve as a basis for future projects in the environmental area, especially as regards the improvement in the treatment of leachate, its reuse as a source of nutrients for growing plants with energy potential. The lack of specific research using soybean and sunflower, irrigated with treated slurry, creates a perspective for the
study and application of this process of reutilization of treated effluent for irrigation of energy crops.

2 Materials and Methods

Before the application in the wetlands, the leachate was treated at the landfill wastewater treatment plant, which included the steps: anaerobic lagoon, facultative lagoon, aerated lagoon and physical-chemical treatment. Results of preliminary analyzes indicated that the treated leachate had organic matter, nitrogen and phosphorus suitable for the use in wetlands. The metals present in the treated leachate were determinated and quantified using Plasma Optical Emission Spectrometry (PerkinElmer Optima 8300).

The plants used in wetlands were soybean and sunflower because they have great potential to generate oil that can transformed into biodiesel.

It was constructed 9 wetlands with 8L each, were filled with a gravel number 3 (5cm of height) and sand (15cm of height). To the removal of the leachate were used valves installed in the lower part of the wetlands, and they were operated in batch mode with hydraulic detention time (HRT) of 2 and 4 days. The concentrations of effluent treated used were 10% and 25% (applied in 3 wetlands for each concentration), both concentrations was determined by laboratory toxicity tests. The liquid chemical fertilizer was applied in other 3 wetlands in concentration of 5 mL / L, added every 20 days, the other irrigation was performed only with water. Each wetland was received 3 liters of the treated effluent per irrigation.

In HRT 2-day, twelve samples were collected for each concentration, and were analised parameters such as: Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (NTK), ammonia (NH₃), nitrate (NO₃⁻), nitrite(NO₂⁻) and total phosphorus (PT), according with APHA (2005).

In the tests carried out with HRT of 4 days, eighteen samples were collected for each concentration. Due to the small amount of sample at the end of each irrigation
cycle, only COD and NH₃ were monitored in this condition, according to the methodologies described in APHA (2005).

After 4 months, the development of the plants was analyzed comparing the wetlands irrigated with leachate and wetlands irrigated with chemical fertilizer.

3 Results and discussion

The table 1 presented the average concentrations of NO₂⁻, NO₃⁻, NH₃, COD, BOD and PT found in treated leachate before to dilutions and applications in wetlands.

Table 1 – Characteristics of the treated leachate collected in the landfill

| Parameter | Average concentration (mg/L) |
|-----------|-------------------------------|
| NO₃⁻      | 11,5                          |
| NO₂⁻      | 1,41                          |
| NH₃       | 21,3                          |
| DQO       | 803,88                        |
| DBO       | 11,00                         |
| PT        | 13,07                         |
| TKN       | 504,00                        |

The characterization of the treated leachate showed that it had potential to be used in the irrigation of the wetlands, because it has high concentrations of phosphorus and COD remaining, which could be used as nutrients in the growth of crops for energetic purposes, would promote a post treatment to leachate improving your final characteristics.

The metals concentrations presents in the leachate collected at the end of the landfill treatment plant are presented in Table 2.
Table 2 – Metals concentrations in leachate landfill and respective standards according to CONAMA 430/11 resolution

| Metals | Concentration (mg/L) | CONAMA 430/2011 (mg/L) |
|--------|----------------------|------------------------|
| Al     | 1,45                 | 10                     |
| Ba     | nd                   | 5                      |
| Cd     | nd                   | 0,2                    |
| Co     | 0,017                | 0,05                   |
| Cr     | 0,031                | 1                      |
| Cu     | nd                   | 1                      |
| Fe     | 0,050                | 15                     |
| Mn     | 0,618                | 1                      |
| Ni     | 0,045                | 2                      |
| Pb     | 0,013                | 0,5                    |
| Zn     | nd                   | 5                      |
| B      | 0,581                | 5                      |
| Li     | 0,053                | 2,5                    |

The metals analyzed in the treated leachate were in concentrations below the limit established by the CONAMA 430/2011 resolution, making it possible to reuse them for the cultivation of energetic plants. Furthermore, the dilutions used in this work greatly reduce the risk of soil contamination where will be applied.

In the experiments with soybean, in both HRT tested, the seeds did not develop in the wetlands. According to Aguiar (1978), Wetzel (1978) and Souza (1996), soybean seeds have membrane more permeable, facilitating its liquid saturation and causing the rupture of the seed. In addition, soybean seed needs to absorb at least 50% of its weight in water to ensure good germination. At this stage, the soil water content should not exceed 85% of the maximum available water and should not be less than 50% (Lantmann, 2014). In the wetlands studied the amount of liquid exceeded 85%
since there was excess of liquid in the surface, being able to be the cause of the non-development of the soybean seeds.

The mean results, and respective standard deviations in parentheses, of the parameters analyzed in the wetlands operated with HRT of 2 days and cultivated with sunflower was show in Table 3.

Table 3 - Initial and final average concentrations of the analysed parameters in the wetlands cultivated with sunflower and operated with HRT of 2 days, their removal percentage and standard deviations

| Leachate concentration (%) | Parameter | Initial concentration (mg/L) | Final concentration (mg/L) | Remotion (%) |
|----------------------------|-----------|------------------------------|----------------------------|--------------|
|                            | COD       | 238,71 (±90,8)              | 180,55 (±45,2)             | 24,4         |
| 25                         | NH₃       | 2,27(±0,23)                 | 0,27(±0,81)                | 88,1         |
|                            | NO₃⁻      | 8,39(±1,12)                 | 23,54 (±8,1)               | -180,5       |
|                            | NO₂⁻      | 0,02(±0,01)                 | 0,01(±0,01)                | 50           |
|                            | PT        | 0,08(±0,005)                | 0,04(±0)                   | 50           |
|                            | TKN       | 146,0(±1,0)                 | 131,4 (±1,2)               | 10           |
|                            | COD       | 184,52(±20,02)             | 79,61 (±35,19)             | 56,9         |
| 10                         | NH₃       | 1,94(±0,06)                 | 0,46(±0,69)                | 76,3         |
|                            | NO₃⁻      | 5,79(±0,91)                 | 22,69 (±8,55)              | -291,9       |
|                            | NO₂⁻      | 0,037(±0,03)                | 0,03(±0)                   | 18,9         |
|                            | PT        | 0,05(±0,005)                | 0,03(±0)                   | 40           |
|                            | TKN       | 102,48(±0,4)                | 100,5(±0,0007)             | 1,9          |

Removal of phosphorus, ammonia, nitrite and TKN was higher when the wetlands were irrigated with treated leachate at 25%. The plants consume phosphorus, mainly in the time of the flowering, being necessary the vegetation removal, because the phosphorus can return to the system later, due to the decay of
the plant. Phosphorus adsorption by the wetland is limited, so when this limit is reached, phosphorus elimination is reduced (Soares, 2012).

In the wetlands, the nitrogen removal occurs from the sequential processes of nitrification and denitrification in aerobic/anoxic environments. After these reactions, the ammoniacal nitrogen is converted into molecular nitrogen, which is released into the atmosphere as gas (Haandel et al., 2009). Nitrogen conversion occurs in three processes: ammonification (or assimilation of ammonia); nitrification and denitrification (Haandel et al., 2009). It was observed an increase in the nitrate concentration in the wetlands percolated, the occurrence of this phenomenon is due that the nitrate is not adsorbed by the substrate where the oleaginous plants were cultivated, due to its negative charge. A portion of this nitrate have been used by the plants for its development and the excess was eliminated with the effluent. Studies conducted by Dutra et al. (2012) evaluating the influence of irrigation on sunflower cultivation showed that this condition of moisture saturation leads to a lack of oxygen to the roots. This condition causes the death of the root tissues, favoring the lactic fermentation and acidosis in the cells, the reduction in nutrient absorption, water and influence the final size of the plant. The HRT may have influenced in the removal efficiency of the analyzed parameters, since the constant watering made the wetlands remain with high humidity. Excess water contributed to the low removal of organic matter from the 25% concentration as compared to the 10% concentration tested, because it may be in the form of recalcitrant compounds and require a higher HRT for the reduction of its concentration. The mean results, and respective standard deviations in parentheses, of the parameters analyzed in the wetlands operated with HRT of 4 days and cultivated with sunflower was show in Table 4.
Table 4 - Initial and final average concentrations of the analysed parameters in the wetlands cultivated with sunflower and operated with HRT of 4 days, their removal percentage and standard deviations

| Leachate concentration (%) | Parameter | Initial concentration (mg/L) | Final concentration (mg/L) | Removal (%) |
|----------------------------|-----------|-----------------------------|---------------------------|-------------|
| 25                         | COD       | 252,7 (±29,7)               | 84,1 (±22,2)              | 66,6        |
|                            | NH₃       | 22,5 (± 1,4)                | 0,22 (±0,09)              | 99,0        |
| 10                         | COD       | 101,1 (±11,8)              | 38,1 (±3,2)              | 62,2        |
|                            | NH₃       | 9,1 (± 1,0)                | 0,15 (±0,08)              | 98,3        |

High HRT caused water and nutritional shortages, favoring high ammonia and COD removal in studied concentrations, being higher when the applied leachate concentration was 25%.

The Table 5 presents the sunflower plants development.

Table 5 - Height of sunflower plants

| HRT (d) | Leachate concentration (%) | Plant height (cm) |
|---------|-----------------------------|-------------------|
|         | 10                          | 20                |
| 2       | 25                          | 17                |
|         | Chemical fertilizer         | 33                |
| 4       | 10                          | 73                |
|         | 25                          | 54                |
|         | Chemical fertilizer         | 55                |

It was observed that the low concentration of leachate (10%), combined with the high HRT (4d), resulted in larger plants, confirming the negative influence of the excess of recalcitrant organic matter and excess moisture in the plant growth.
4 Conclusions

The application of treated leachate at 10% concentration and with HRT of 4 days favored the treatment of the effluent and the growth of the sunflower plants.

The HRT of 2 days maintained the wetlands with excess humidity, damaging its efficiency and the growth of cultivated plants.

The treated leachate presented an improvement in its quality after passing through the wetlands, indicating the possibility of this reuse for the sunflower seed cultivation that can be used to obtain biofuels.

Acknowledgements

Thanks to the reviewers and the Santa Catarina State University.

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