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ANALYSIS OF A WETLAND SYSTEM IN THE POST-TREATMENT OF WASTEWATER

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Abstract

The study was based on a surface flow wetland system, using the macrophyte *Eicchornia crassipes*. The use of wetlands as an alternative in the wastewater treatment process has been employed due to the handling and simple technology, addition to the low cost compared to conventional systems. Three hydraulic retention times, they are 4, 6 and 8 days were analyzed. In general the system showed significant results in relation to removals of nutrients for all TRH reviews, where the hydraulic retention time of 6 days achieved the best performance. The proposed system achieved 79.91% reductions for COD, 83.51% of Total Phosphorus, Total Nitrogen 67.93%, 87.7% chromium and 52% Sulfur.

Key-words: Wetland, aquatic macrophytes, wastewater.

ANÁLISE DE UM SISTEMA WETLAND NO PÓS-TRATAMENTO DE ÁGUAS RESIDUAIS

Resumo

O estudo foi baseado em um sistema wetland de fluxo superficial, utilizando-se a macrófita aquática *Eicchornia crassipes*. O uso de wetlands como alternativa no processo de tratamento

de águas residuais vem sendo empregado devido ao manejo e tecnologia simples, além do baixo custo em relação a outros sistemas convencionais. Foram avaliados três tempos de retenção hidráulica, sendo eles 4, 6 e 8 dias. De modo geral o sistema apresentou resultados significativos em relação a remoções de nutrientes para todos os TRH avaliados, onde o tempo de retenção hidráulica de 6 dias obteve o melhor desempenho. O sistema proposto obteve reduções 79,91% para DQO, 83,51% de Fósforo total, 67,93% de Nitrogênio total, 87,7% de Cromo e de 52% de Enxofre.

Palavras-chave: Wetland, Macrófitas aquáticas, águas residuais.

Introducion

Technologies of wastewater treatment in built flooded areas have been used since 1970. These techniques are based not only on biotic processes that contemplate the action of microorganisms and nourishment absorption by the plants introduced in solution at the environment, but also they contemplate abiotic process that include chemistry precipitation, sedimentation and adsorption of ions on the substrate (Lin et al, 2005; Álvarez & Bécare 2008; Tang et al 2009).

The built *wetland* are systems artificially projected to use aquatic plants (macrophyte) on substrates such as sand, graves or any other inert material, on which occurs the proliferation of biofilms that aggregate several populations of microorganism, which, through biological, chemical and physical process, treat the wastewater. They are distinguished for presenting moderated capital cost, low energy consumption and maintenance, landscapes aesthetics and increase of wildlife habitat (IWA, 2000; Ruan et al., 2006; Hedmark et al., 2009; McJannet et al., 2012).

Build wetlands imitate natural swamps, recently being amongst the most effective wastewater treatment. They have been used as a low cost alternative for secondary and tertiary conventional sewage treatment. There are three types of built wetland: Superficial Flow, Integrated Vertical Flow and Subsurface Flow. Opposed to the superficial flow systems and the integrated vertical, there is the subsurface flow, which its investment and operation cost are lower, however, it occupies larger structural areas, besides presenting reduced efficiency regarding the treatment when compared to the others (Ruan et al., 2006; Chen et al., 2008; Jou et al., 2009).

Considering the industrial wastewater, the ones derived from the leather industry stand out. According to Imhoff (1985), wastewater from tannery is highly polluted. Besides having putrescible substances, they contain toxic salts, alkalis and sulfur compounds. Tannery presents high water consumption, from 25 to 30m³ per ton of salted skin or 630 L/salted skin, in average, that varies according to the processes used, according to the management, and other factors.

A midsize tannery that process 3.000 salted skins.day^{-1}, consume roughly 1.900 m³ water.day^{-1} ,which is equivalent to the diary consumption of a population with 10.500 inhabitants. Therefore, the average consumption per capita would be 180L.day^{-1} (Pacheco, 2005).

Considering the environmental problems caused by the leather industry, the goal of this paper was to evaluate the nourishment absorption in a wetland system built on a pilot scale, using macrophyte *Eicchornia crassipes* on the post treatment of tannery effluents, in view of enlightening the hypothesis that the system will reduce the high load of pollutants.

Material e methods

The present work is about a toxicological testing and operation of a wetland system on a pilot scale, installed and conducted in the city of Toledo – PR, located in the geographical coordinates 24º43'26''S and 53º45'11''W. The system is constituted of a superficial flow wetland, compounded by a battery of four tanks, shaped like gutters, presenting usable volumes of 215L each gutter (Figure 1), using macrophyte *Eicchornia crassipes* and operated with tannery effluents located at the region (Chen et al., 2008; Álvarez & Becares 2008; Hu & Shan, 2009).

The choice of macrophyte, used in this test, was based on the information collected from the scientific literature, evaluating its level of absorption and its growth. They were weighted and a accommodated in a density of 5,9 kg.plant.m^2 of liquid surface (Espinoza-Quinoñes et al., 2005; Ruan et al., 2006; Chen et al., 2008; Cui et al., 2008; Hu & Shan, 2009).
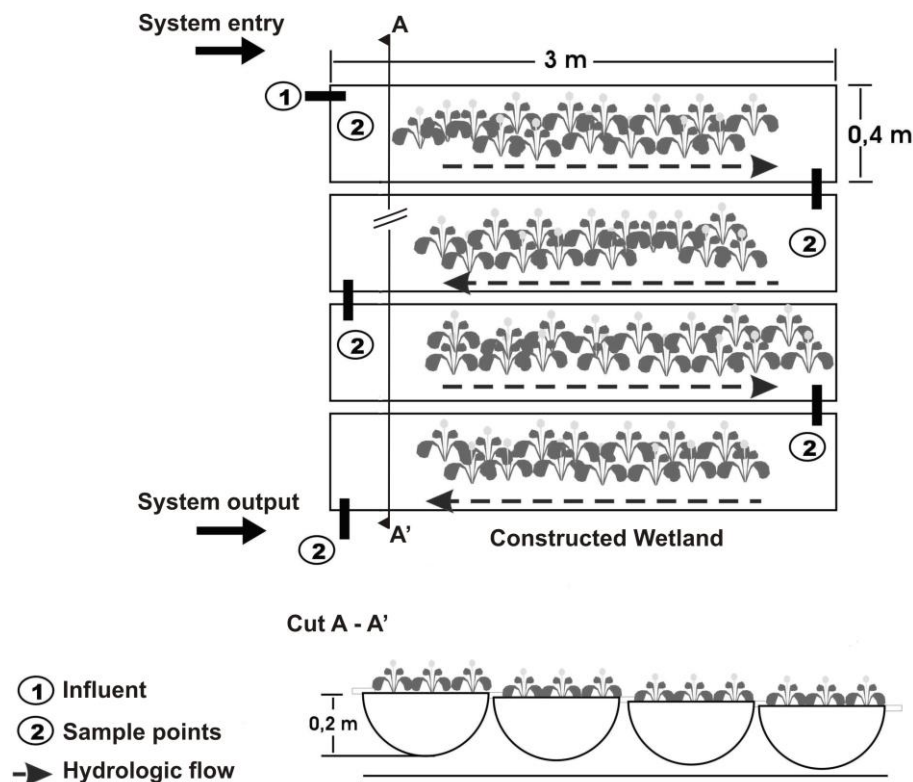
Figura 1.　　　Wetland system detailing on a pilot scale.

　　　The toxicological testing of this work was performed considering the goal of finding the most adequate effluent concentration to the tolerance of the *macrophyte* chosen for the study. The dilutions tested were: raw tannery effluent, ¾ (75%), ½ (50%) 1/5 (20%) and 1/10 (10%). The design applied on this test was entirely randomized (DIC), on which, it was evaluated the *macrophyte* survival rate within the period of seven days, performed in rejoinders, submitted to analysis of variance and the averages compared by Tukey test, 5% significance (Espinoza-quinones et al., 2005; Espinoza-Quiñones et al., 2008; Hu & Shan 2009).

　　　Once the toxicological test was performed, the evaluation of the wetland system was started, on which three Hydraulic Retention Times were tested (HRT). They were: 4, 6 and 8 days for 5 weeks each time. The evaluated parameters on this test were: pH, Temperature, Total Nitrogen, COD, Total Phosphor, according to Standad Metods (APHA, 2005), and Chrome and Sulfur were evaluated by the X-Ray Fluorescence technique, known as XRF (Espinoza-Quiñones et al., 2008).

In this technique, the amount of metals dissolved in the effluents are evaluated with accuracy, considering a aliquot of 60 mL for each sample, separated and filtrated through a Milipore filtration system with a 47 mm membrane of diameter of cellulose acetate with pores of 0,45 μm. After filtrating, in each 10mL alíquota from each sample, it was added 10 μL of yttrium solution (Y 11,6 g/l^{-1}), as internal standard. 5 μL aliquots were deposited in the pre-cleaning of acrylic discs (ø☐ 32mm, 3mm thickness) and dried at room temperature. For the XRF analysis, the samples with dry wastes were irradiated with a polychromatic X-ray beam with maximum energy of 20 keV, at the Synchrotron Light National Laboratory (translated from the Portuguese and stands for *Laboratório Nacional de Luz Síncrotron* - LNLS), in Campinas, São Paulo, Brazil. The X-ray spectrums were analysed using AXIL software. Using a calibration curve for the XRF system, the concentrations of the metals dissolved in the effluents were determined. The sample points were taken by the end of each gutter from the system, performed in rejoinders, in order to provide the statistic treatment.

Results and discussion

Toxicological Tests

Amongst the concentrations tested during the toxicological test, it was chosen to operate with effluents diluted ½ (50%), because they presented better survival and tolerance conditions for the effluent tested, not presenting significant difference ($p>0,05$) among the samples. In concentrations with higher dilution (more than ½ or 50%), *macrophyte* presented higher mortality, with significant difference ($p >0,05$), according to the test of Tukey.

Characterization of the effluent

Table 1 presents the average concentration values of the parameters analyzed for the chosen effluent during the experiment performance.

Tabela 1. Characterization of the effluent worked post-process of wastewater treatment applied at the studied tannery. Average values in mg.L^{-1} sampled during the HRT evaluated.

Parameter	HRT 4 days	HRT 6 days	HRT 8 days	Average
COD	1010 $\pm$ 464	618 $\pm$ 497	868 $\pm$ 378	832 $\pm$ 198
Total Nitrogen	1,17 $\pm$ 0,14	0,57 $\pm$ 0,16	0,66 $\pm$ 0,04	0,80 $\pm$ 0,32
Total Phosphor	1,47 $\pm$ 0,58	0,34 $\pm$ 0,10	0,48 $\pm$ 0,22	0,76 $\pm$ 0,62
Dissolved O_2	5,40 $\pm$ 1,80	2,87 $\pm$ 2,11	4,53 $\pm$ 3,46	4,27 $\pm$ 1,29
pH	6,53 $\pm$ 0,6	6,21 $\pm$ 0,14	7,10 $\pm$ 0,7	6,61 $\pm$ 0,37
Temperature (ºC)	27 $\pm$ 3	26 $\pm$ 6	25 $\pm$ 4	26 $\pm$ 0,6
Chrome (Cr)	0,47 $\pm$ 0,07	0,54 $\pm$ 0,21	1,24 $\pm$ 0,23	0,74 $\pm$ 0,42
Sulfur (S)	733 $\pm$ 102	1113 $\pm$ 501	937 $\pm$ 75	928 $\pm$ 190

$\pm$ Standard deviation

Some parameters analyzed presented large variation among the different treatments applied, as well as, during the performance of each treatment. For the Chemical oxygen demand (COD), for example, variation were observed in a range from 618 to 1010 mg.L^{-1} between the times studied, as well as the Total Nitrogen and Total Phosphor, which presented variation from 1,17 to 0,66 mg.L^{-1} and 1,47 to 0,34 mg.L^{-1} respectively. Pacheco (2005) evaluated the national average concentration of Total N for gross emission of effluents from the leather processing industry and observed values between 0,1 and 0,2 mg.L^{-1} Total N for tanning of leather semi-finished. Studies performed by Cui et al., (2008) using wetland systems to remove nourishments showed that there was a loss of efficiency due to alterations of the nourishments concentration.

Performance of the system on a pilot scale

Results regarding the performance of the system considering the evaluated parameters are displayed on Figure 2.
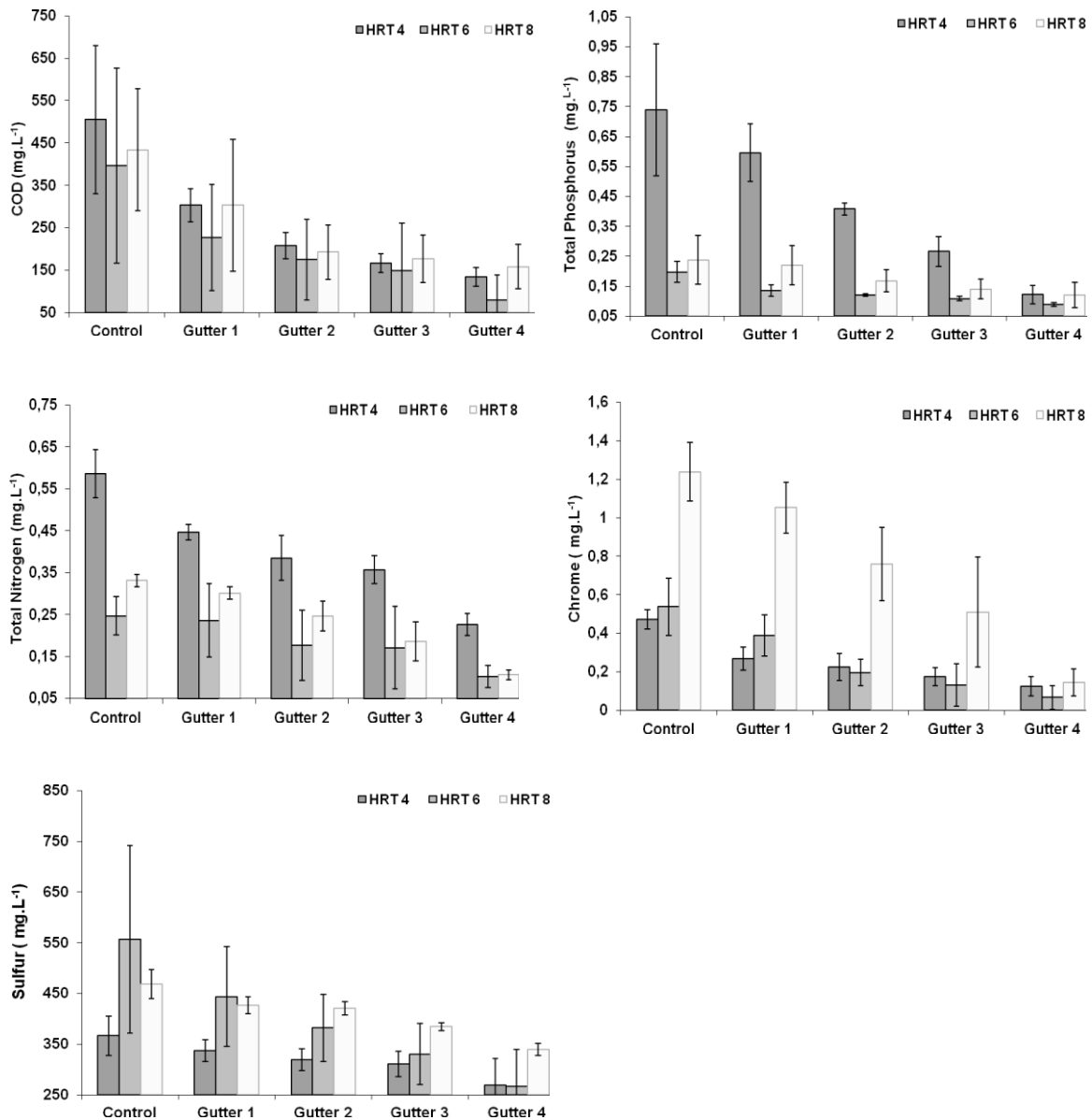
Figura 2. Effluent performance along the treatment system applied. Average values in mg.L^{-1} sampled during the HRT evaluated.

Chemical Oxygen Demand – COD

Regarding the COD reduction, it can be observed that the removal obtained was similar for every retention time evaluated, with reductions of 73,4%, 79,9% and 63,5% for the HRT 4, 6 and 8 days, respectively, where the higher reduction observed was on HRT 6 days. Some researchers observed similar results when evaluation built wetlands, testing not only emergent plants such as *Phragmites communis* and *Typha orientalis*, but also floating plants such as *Pistia stratiotes* and *Eichhornia crassipes*. Regarding the results obtained, the

removal of carbonaceous matter, expressed as COD, of 64% to 97% evaluated in retention times of 2, 4, 5 and 7 days (Chen et al., 2008; Jou et al., 2009).

For the three retention times evaluated, the performance was similar, presenting significant reduction in the two first gutters (> 50%), where the final organic load remained between $80 - 158$ mg.L^{-1} COD, therefore, within the acceptable levels imposed by the current legislation (CONAMA, 2005).

Phosphor

Phosphor does not present sanitary problems in water supplies, but it is the effluent constituent that is more associated to the eutrophication of superficial water, where its disposal is limited to 0,1 mg.L^{-1} of total phosphor for disposal at lotic environments and tributaries of intermediary environments (CONAMA, 2005). On the evaluation of the total phosphor by the proposed system, it presented similar efficiency of removal at 6 and 8 days with reductions of 54,8% and 49,2% of the initial concentration, achieving 83,5% in 4 days. However, despite of the significant reduction, the system is ineffective for the treatment of this parameter, exceeding the maximum load tolerated by the legislation.

In a study using the constructed wetland for removal of P, was observed that the percentage reduction in the nutrient decreased from 82% to 33.2%, due to variations in the concentration in the initial system entry (Cui et al., 2008).

Total Nitrogen

The form that nitrogen incorporates the biomass of *macrophyte* is by assimilation. This process refers to a variety of biological processes that convert inorganic forms of nitrogen into organic compounds. These compounds work as a reservoir for the cell and tissues of the plants (Kadlec et al, 2000). For total nitrogen, the reduction observed at the system was 61,4%, 58,7% and 68%, for the times of 4, 6 and 8 days respectively. Similarly to COD and total phosphor, the initial concentration of the effluent for the HRT 4 days was higher than the other times evaluated. However, it did not interfered the performance of the system, where the final concentrations of total nitrogen were from 10 to 0,22 mg.L^{-1} of Total N. Similar results were obtained in two wetland systems, one with superficial flow and the other with subsurface flow, with wastewater contaminated by nitrate, on which, reductions between 60% and 85% were observed (Sousa, et al., 2003; Ying-Feng et al., 2008).

Despite of the removal obtained, higher concentrations of nourishment can limit the rate of nitrate removal from a biological process of denitrification (USEPA, 2000;Tang et al., 2008; Tang et al., 2009).

Chrome

Chrome is the main problem of tannery, because it is the input used by most of the companies in the tanning process. This is one of the human activities mainly responsible by its release to the environment (Hafez et al, 2002; Pacheco, 2005). Chrome has its release limited to 0,55 mg.L^{-1} of Cr for effluent emissions of any type of source in water bodies (CONAMA, 2005).

According to Figure 2, at the end of all retention times that were evaluated, chrome presented results within the standard of effluent emission, currently established, on which the reductions obtained were 73,7%; 87,7% and 88,3% for HRT 4, 6 and 8 days, respectively. By the end of the system, the effluent presented concentrations between 0,065 to 0,14 mg.L^{-1} of Cr, similar to the ones obtained by studies performed by Pacheco (2005), between 0,1 to 0,2 mg.L^{-1} of Cr for emissions preliminary post-treatment, primary treatment or physical-chemical and biological treatment.

Chrome toxicity depends of the oxidation state on which it is disposed in the effluent. Most of its soluble compounds, in superficial water, can be presented as hexavalent chrome (Cr^{+6}), and a small part as chrome (Cr^{+3}) in organic complexes. Hexavalent chrome can, however, be reduced to chrome (Cr^{+3}) by organic matters existent in the water and can, eventually, deposit itself on the sediments. Chrome assimilation by *macrophytes* can be also considered, once many metals are required for their growth (traces) (Knox et al., 2006; Espinoza-Quinoñes et al., 2008).

Sulfur

Sulfur, as sulfide, also exists in the tannery disposal and it is a high toxicity compound that brings discomfort at the treatment installations. Soluble in alkaline aqueous solutions, with the lowering of pH values, sulfide ion is connected to the hydrogen ion existent in the solution, forming H_2S, hydrogen sulfide, hydrogen sulfide or hydrogen sulfide (Pacheco, 2005). At the treatment system proposed, the results regarding the final concentrations of sulfur were 269,51, 267,30 and 339,58 mg.L^{-1} for HRT 4, 6 and 8 days,

respectively. Between the evaluated retention times, HRT 6 days presented the best result, with 52% reduction, meanwhile, HRT 4 and 8 days presented reduction of 26,5 and 27,6%.

Amongst the parameters evaluated on the experiment, sulfur as sulfide ion was the one that presented the lowest reduction rate, which can be explained by its high concentration on the system (Kadlec, et al., 2000; Cui et al., 2008). Sulfide, existent in the effluents of the tannery treatment, is the most toxic compound for the human being, more toxic then chrome from tannery, considering that the last one is in its trivalent form (Pacheco, 2005).

Conclusions

Altogether, the hydraulic retention time of 6 days was the one that presented better results on the removal of the parameters evaluated, presenting satisfactory results regarding the removals, being within the limits established by the current legislation for effluent disposal from polluting sources.

For total phosphor and sulfur, the system was not proved to be effective, not being able to reach the minimal standards of disposal, for these nourishments.

The system presented operational limitations with the tannery effluent used, considering the large variation of composition and high initial concentrations of operation, especially for sulfur.

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